Bridging the gap between modelled and observed SOA: implications from chamber simulation and field campaigns

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Secondary Organic Aerosols (SOA)

- Gap between modeled and measured SOA: models underestimate SOA by a factor up to 10.

(Volkamer et al., 2006, GRL; de Gouw and Jimenez, 2009, EST)
SOA Observed
(offline: EC-tracer; online: AMS-OOA)

\[ OC_{pri} = (OC/EC)_{pri} \times EC \]

\[ OC_{sec} = OC_{tot} - OC_{pri} \]

OC/EC from biomass burning

**Wood burning**
- 2.3 – 23.0 \( \text{(12.7)} \)  Fine at al., 2001  (Northern US)
- 5.6 – 61.8 \( \text{(23.4)} \)  Fine et al., 2002  (Southern US)

**Cereal straw burning**
- OC/EC > 7  (Zhang et al., 2007)
SOA observed by tracer methods

\[ \Delta \text{SOC} = \text{SOC}_{\text{EC-tracer}} - \text{SOC}_{\text{SOA-tracer}} \]

Overestimated under the influence of biomass burning

(Ding et al., JGR, 2012)
Table 15. Major Differences in BC and OC Predicted by Current and Previous Emission Factors (in Order of Greatest Absolute Difference in BC Inventory)\textsuperscript{a}

<table>
<thead>
<tr>
<th>Fuel/Sector</th>
<th>Black Carbon</th>
<th></th>
<th>Organic Carbon</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This Work</td>
<td>Previous96</td>
<td>Difference</td>
<td>This Work</td>
</tr>
<tr>
<td>Open burning</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Open burning/forest</td>
<td>1238</td>
<td>2966</td>
<td>-1728</td>
<td>11,239</td>
</tr>
<tr>
<td>Open burning/savanna</td>
<td>1715</td>
<td>2894</td>
<td>-1179</td>
<td>12,147</td>
</tr>
<tr>
<td>Open burning/crop resid</td>
<td>328</td>
<td>356</td>
<td>-28</td>
<td>1567</td>
</tr>
<tr>
<td>Contained combustion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal/power generation</td>
<td>7</td>
<td>1606</td>
<td>-1599</td>
<td>5</td>
</tr>
<tr>
<td>Diesel fuel/on-road</td>
<td>792</td>
<td>2179</td>
<td>-1387</td>
<td>292</td>
</tr>
<tr>
<td>Wood/residential</td>
<td>880</td>
<td>1921</td>
<td>-1041</td>
<td>3506</td>
</tr>
<tr>
<td>Agricultural waste/residential</td>
<td>393</td>
<td>90</td>
<td>303</td>
<td>1492</td>
</tr>
<tr>
<td>Animal waste/residential</td>
<td>208</td>
<td>417</td>
<td>-209</td>
<td>750</td>
</tr>
<tr>
<td>Coal/industry\textsuperscript{b}</td>
<td>642</td>
<td>1181</td>
<td>-539</td>
<td>450</td>
</tr>
<tr>
<td>Diesel fuel/residential</td>
<td>85</td>
<td>369</td>
<td>-284</td>
<td>28</td>
</tr>
<tr>
<td>Coal/residential</td>
<td>480</td>
<td>761</td>
<td>-281</td>
<td>422</td>
</tr>
<tr>
<td>Diesel fuel/off-road</td>
<td>579</td>
<td>691</td>
<td>-112</td>
<td>288</td>
</tr>
<tr>
<td>Gasoline/transport</td>
<td>125</td>
<td>50</td>
<td>75</td>
<td>904</td>
</tr>
<tr>
<td>Other</td>
<td>478</td>
<td>524</td>
<td>-46</td>
<td>776</td>
</tr>
<tr>
<td>Total</td>
<td>7950</td>
<td>16,005</td>
<td>-8055</td>
<td>33,866</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Units are Gg/yr based on 1996 fuel-use data (for contained combustion) or annual averages (for open burning).

\textsuperscript{b}Includes coking, which accounts for 380 Tg BC, 270 Tg OC in this work; 320 Tg BC, 320 Tg OC in Previous96.
SOA observed

Organic acids

Many OOA might be primary
LV-OOA: Sulfate
SV-OOA: Nitrate
HOA: NOx, EC
COA: C₅H₈O⁺, C₆H₁₀O⁺, C₇H₁₂O⁺
BBOA: levoglucosan
CCOA: ……
NOA:……

mz 44: OOA
mz 41, 43, 55, 57: HOA

Online VS Offline?
Predicted SOA matched the observed in chamber studies?

Chamber studies: emission and meteorological factors are excluded
SOA formation from individual VOC in SMOG chamber

Two product model

Odum et al., 1996; Ng et al., 2007; Wang et al., 2014
SOA formation from gasoline vapor in chamber

• SOA yield curves of 17 individual aromatic species from smog chamber gasoline experiments.
• These yield curves, interpreted within the framework of a gas/aerosol absorption model, are used to quantitatively account for the SOA that is formed from the whole vapor of 12 different reformulated gasolines.
• The total amount of secondary organic aerosol produced from the atmospheric oxidation of whole gasoline vapor can be represented as the sum of the contributions of the individual aromatic molecular constituents of the fuel.
SOA formation from whole gasoline vapor in chamber

The Atmospheric Aerosol-Forming Potential of Whole Gasoline Vapor

J. R. Odum, T. P. W. Jungkamp, R. J. Griffin, R. C. Flagan, J. H. Seinfeld

A series of sunlight-irradiated, smog-chamber experiments confirmed that the atmospheric organic aerosol formation potential of whole gasoline vapor can be accounted for solely in terms of the aromatic fraction of the fuel. The total amount of secondary organic aerosol produced from the atmospheric oxidation of whole gasoline vapor can be represented as the sum of the contributions of the individual aromatic molecular constituents of the fuel. The urban atmospheric, anthropogenic hydrocarbon profile is approximated well by evaporated whole gasoline, and thus these results suggest that it is possible to model atmospheric secondary organic aerosol formation.

Table 2. Properties of AQIRP reformulated gasolines. MTBE = the fuel additive methyl tertiary butyl ether; the fuel identification code is derived from A (a) = high (low) aromatics, M (m) = high (low) MTBE, O (o) = high (low) olefins, T (t) = high (low) T<sub>20</sub>, RMH = medium and heavy reformate cut (predominantly C<sub>9</sub> and C<sub>10</sub> aromatics), and AH = heavy alkylate cut (heavy paraffins).

<table>
<thead>
<tr>
<th>Fuel code</th>
<th>AROMIRP phase</th>
<th>Fuel ID</th>
<th>Aromatics (vol %)</th>
<th>MTBE (vol %)</th>
<th>Olefins (vol %)</th>
<th>T&lt;sub&gt;20&lt;/sub&gt; (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>I</td>
<td>Industry average</td>
<td>32.0</td>
<td>0.0</td>
<td>9.2</td>
<td>166</td>
</tr>
<tr>
<td>F</td>
<td>I</td>
<td>amot</td>
<td>20.0</td>
<td>0.0</td>
<td>3.2</td>
<td>137</td>
</tr>
<tr>
<td>G</td>
<td>I</td>
<td>AmOt</td>
<td>44.3</td>
<td>0.0</td>
<td>17.4</td>
<td>141</td>
</tr>
<tr>
<td>K</td>
<td>I</td>
<td>Amot</td>
<td>45.7</td>
<td>0.0</td>
<td>4.9</td>
<td>146</td>
</tr>
<tr>
<td>L</td>
<td>I</td>
<td>AmOT</td>
<td>47.8</td>
<td>0.0</td>
<td>17.7</td>
<td>181</td>
</tr>
<tr>
<td>O</td>
<td>I</td>
<td>AMOt</td>
<td>46.7</td>
<td>14.6</td>
<td>19.3</td>
<td>139</td>
</tr>
<tr>
<td>P</td>
<td>I</td>
<td>amOt</td>
<td>20.3</td>
<td>0.0</td>
<td>18.3</td>
<td>140</td>
</tr>
<tr>
<td>C2</td>
<td>II</td>
<td>California phase II</td>
<td>25.4</td>
<td>11.2</td>
<td>4.1</td>
<td>145</td>
</tr>
<tr>
<td>1B</td>
<td>II</td>
<td>Matrix B base</td>
<td>25.3</td>
<td>11.2</td>
<td>15.0</td>
<td>131</td>
</tr>
<tr>
<td>2B</td>
<td>II</td>
<td>Base + RMH</td>
<td>35.1</td>
<td>10.4</td>
<td>11.2</td>
<td>157</td>
</tr>
<tr>
<td>3B</td>
<td>II</td>
<td>Base + AH</td>
<td>22.1</td>
<td>10.4</td>
<td>13.3</td>
<td>148</td>
</tr>
<tr>
<td>4B</td>
<td>II</td>
<td>Base + AH + RMH</td>
<td>32.2</td>
<td>10.2</td>
<td>10.7</td>
<td>168</td>
</tr>
</tbody>
</table>
Matrix effect: purified air VS ambient air
SOA from “SO$_2$+NO$_x$+toluene”

Ng et al., 2007; Hildebrandt et al., 2009; Deng et al., 2017
Combustion sources are important and far more complex with emission of organics from very volatile organic compounds to low- and non-volatile organic compounds that all potentially contribute to SOA formation.

Globally important: biomass burning

Important in urban areas: vehicle exhaust (diesel in particular)

SOA formed from these important sources can be predicted with traditional precursors?
GIG Smog chamber (30m³)

Gas/Dies
Vehicle exhaust

C/W/R
Biomass burning
Experimental design

30 m³ smog chamber

- Dark characterization
- Photo-oxidation

Primary
- BC/BrC
- POA

Secondary
- SOA, ......
Biomass burning: open or quasi-open combustion of any non-fossilized vegetative or organic fuel

(Andreae and Merlet, 2001, GBC; Akagi et al., 2011, ACP)
More than 90% of global primary organic carbon
More than 60% of global black carbon

(Bond et al., *JGR*, 2004)
Biomass burning: globally important pollution source

Biomass burning: the largest BC and OC source

Global OC emission

(Bond et al., 2013, JGR; Huang et al., 2015, AE)
Secondary organic aerosol budget

BBSOA: 71% in global SOA burden

Global seasonal SOA production: peaks when BB is at its maximum in the North Hemisphere

(Tsigaridis et al., 2014, ACP; Shrivastava et al., 2015, JGR)
SOA mass prediction

Aromatic and biogenic hydrocarbons: explain <20% formed SOA in oak and pine burning plume

22 NMOGs (11 containing O): explained 84-116% formed SOA in beech burning plume

How about agricultural residue burning?

(Grieshop et al., 2009, ACP; Bruns et al., 2016, Sci. Rep.)
### Previous chamber work on BBSOA

<table>
<thead>
<tr>
<th>Author</th>
<th>Year</th>
<th>Fuels</th>
<th>Relative humidity (%)</th>
<th>UV light</th>
<th>Time (h)</th>
<th>OA enhancement ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grieshop et al.</td>
<td>2009</td>
<td>Pine, oak</td>
<td>~5</td>
<td>Yes</td>
<td>5-6</td>
<td>1.5-2.8</td>
</tr>
<tr>
<td>Heringa et al.</td>
<td>2011</td>
<td>Beech</td>
<td>50</td>
<td>Yes</td>
<td>5</td>
<td>4.1 ± 1.4</td>
</tr>
<tr>
<td>Hennigan et al.</td>
<td>2011</td>
<td>Wildfire fuels</td>
<td>19</td>
<td>Yes</td>
<td>3-4.5</td>
<td>1.7 ± 0.7</td>
</tr>
<tr>
<td>Ortega et al.</td>
<td>2013</td>
<td>16 unique biomasses</td>
<td>30</td>
<td>Yes</td>
<td>3-120</td>
<td>1.4 ± 0.4</td>
</tr>
<tr>
<td>Bruns et al.</td>
<td>2016</td>
<td>Beech</td>
<td>55</td>
<td>Yes</td>
<td>4-6.5</td>
<td>~3-7</td>
</tr>
<tr>
<td>Tiitta et al.</td>
<td>2016</td>
<td>Birch, beech, spruce</td>
<td>60 ± 5</td>
<td>Yes/No</td>
<td>4.5-16</td>
<td>1.6-2.6</td>
</tr>
<tr>
<td>Tkacik et al.</td>
<td>2017</td>
<td>Pine, spruce</td>
<td>Not reported</td>
<td>Yes/No</td>
<td>~3.5</td>
<td>1.8 ± 0.9</td>
</tr>
</tbody>
</table>

Reported BBOA enhancement ratios during the photoaging process: 0.7-6.8
Corn, Rice, Wheat contributed most to BB emissions in China

Zhou et al., 2017, ACP
SOA precursors—straw burning

\[ \text{SOA}_{\text{predicted}} = \sum_i \Delta X_i \times Y_i \]

Reacted VOC \(\rightarrow\) SOA yield

- Biomass Burning: 20 NMHCs and OVOCs only account for 5.0-27.3% of formed SOA

(Fang et al., 2017, ACP)
Considering unspeciated organics

SOA yield_{unsp} = [Unexplained SOA]/[Unspeciated organics], then SOA surrogate was determined according to the SOA yield_{unsp}

<table>
<thead>
<tr>
<th>Source</th>
<th>SOA surrogate</th>
<th>C_\infty (\mu g \ m^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>Biomass burning/Wood burning</td>
<td>n-pentadecane</td>
<td>0.044</td>
</tr>
<tr>
<td>On- and off-road gasoline</td>
<td>n-tridecane</td>
<td>0.014</td>
</tr>
<tr>
<td>On- and off-road diesel</td>
<td>n-pentadecane</td>
<td>0.044</td>
</tr>
</tbody>
</table>

SOA prediction improved with unspeciated organics accounted:

(Jathar et al., 2014, PNAS)
China overtook USA as the largest auto market in 2010;
Increasing at a rate over 20% per year in the recent years
Passenger cars dominates
Vehicle emission of primary PM: over 90% by diesel

(中国机动车环境管理年报, 2017)
SOA formation from diesel vehicle exhaust

SOA/POA: ~3

(Robinson et al., 2007)
### SOA formation from diesel vehicle exhaust

<table>
<thead>
<tr>
<th>Conditions</th>
<th>country</th>
<th>literatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>idle</td>
<td>USA</td>
<td>Weitkamp et al., 2007</td>
</tr>
<tr>
<td>idle</td>
<td>USA</td>
<td>Robinson et al., 2007</td>
</tr>
<tr>
<td>idle, 60 km/h</td>
<td>Switzerland</td>
<td>Chirico et al., 2010</td>
</tr>
<tr>
<td>idle, UDDS, UC</td>
<td>USA</td>
<td>Gordon et al., 2014; Zhao et al., 2014; 2015</td>
</tr>
<tr>
<td>idle</td>
<td>USA</td>
<td>Presto et al., 2014</td>
</tr>
</tbody>
</table>
SOA from diesel vehicle exhaust

Idle
20 km/h
40 km/h

Diesel
Exhausts

25 °C,
< 5%,
VOC/NOx ≈ 3
### SOA from diesel vehicle exhaust: precursors

\[ SOA_{predicted} = \sum_{i} \Delta X_i \times Y_i \]

**VOC consumed** → yield

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>Benzene (µg m(^{-3}))</th>
<th>Toluene (µg m(^{-3}))</th>
<th>C(_2)-benzene (µg m(^{-3}))</th>
<th>C(_3)-benzene (µg m(^{-3}))</th>
<th>C(_4)-benzene (µg m(^{-3}))</th>
<th>Alkanes (µg m(^{-3}))</th>
<th>Alkenes (µg m(^{-3}))</th>
<th>Predicted SOA/Measured SOA (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.015</td>
<td>0.019</td>
<td>0.022</td>
<td>0.081</td>
<td>0.085</td>
<td>0.022</td>
<td>0.080</td>
<td>2.6%</td>
</tr>
<tr>
<td>2</td>
<td>0.202</td>
<td>0.028</td>
<td>0.050</td>
<td>0.068</td>
<td>0.114</td>
<td>0.002</td>
<td>0.012</td>
<td>2.2%</td>
</tr>
<tr>
<td>3</td>
<td>0.069</td>
<td>0.013</td>
<td>0.051</td>
<td>0.054</td>
<td>0.068</td>
<td>0.038</td>
<td>0.082</td>
<td>1.4%</td>
</tr>
<tr>
<td>4</td>
<td>0.127</td>
<td>0.055</td>
<td>0.013</td>
<td>0.007</td>
<td>0.017</td>
<td>0.028</td>
<td>0.013</td>
<td>0.8%</td>
</tr>
<tr>
<td>5</td>
<td>0.074</td>
<td>0.012</td>
<td>0.082</td>
<td>0.075</td>
<td>0.108</td>
<td>0.030</td>
<td>0.229</td>
<td>1.6%</td>
</tr>
<tr>
<td>6</td>
<td>0.237</td>
<td>0.213</td>
<td>0.496</td>
<td>0.018</td>
<td>0.007</td>
<td>0.029</td>
<td>0.090</td>
<td>3.1%</td>
</tr>
<tr>
<td>7</td>
<td>0.164</td>
<td>0.065</td>
<td>0.014</td>
<td>0.052</td>
<td>0.077</td>
<td>0.049</td>
<td>0.019</td>
<td>1.2%</td>
</tr>
<tr>
<td>8</td>
<td>0.329</td>
<td>0.072</td>
<td>0.067</td>
<td>0.124</td>
<td>0.229</td>
<td>0.052</td>
<td>0.34</td>
<td>2.3%</td>
</tr>
</tbody>
</table>

\(C_2-C_{12} \text{NMHCs} < 3\% \text{ SOA explained;}\)
Aromatic hydrocarbons + PAHs: <10% SOA explained;

OVOCs: 15~45% SOA explained

SOA from diesel vehicle exhaust: precursors

- Aromatics
- PAHs
- OVOCs

![Graph showing SOA predicted vs. measured for different speeds and precursors.]

- At 20 km h⁻¹, OVOCs contribute significantly to SOA, with a measured SOA of around 40%.
- At 40 km h⁻¹, the contribution of OVOCs to SOA is still significant, with a measured SOA of approximately 30%.

✅ Aromatic hydrocarbons + PAHs: <10% SOA explained;
✅ OVOCs: 15~45% SOA explained
SOA from diesel vehicle exhaust: precursors

IVOC: such like $C_{12}$$\sim C_{22}$ alkanes?

- **idle**: $\frac{IVOC}{POA} = 20.4 \pm 3.7$
- **driving**: $\frac{IVOC}{POA} = 8.0 \pm 3.6$

(Sha et al., 2014; Zhao et al., 2015)
SOA from diesel vehicle exhaust: precursors

- IVOC: can explain up to 63-81% of formed SOA.

*Deng et al., in preparation*
SOA from aging of vehicle exhaust

(Gentner et al., 2012, PNAS)

(Jathar et al., 2014, PNAS)
SOA formation from idling gasoline passenger vehicle emissions

- Injecting the vehicle exhaust into the chamber directly;
- SOA Production factor: 0.005 – 0.09 g kg\(^{-1}\); 0.48 g kg\(^{-1}\) for the cold start;
- SOA/POA ratios: 7-510;
- Classic C6-C9 aromatics can explain up to 60% of the formed SOA.

Nordin et al., 2013; ACP
SOA formation from idling gasoline passenger vehicle emissions

- SOA Production factor: 0.001-0.044 g kg$^{-1}$;
- SOA/POA ratios: 12-259;
- Traditional single-ring aromatics and naphthalene can explain 51-90% of the formed SOA.

China vehicles

Liu et al., 2015, ACP
SOA formation from gasoline vehicles during driving cycle

- Pre-LEV, LEV-1, LEV-2; hot-start and cold-start;
- SOA Production factor: 0.02-0.13 g kg\(^{-1}\); SOA/POA ratios: 1-15;
- Except pre-LEV, the SOA production could not be fully explained by the measured traditional SOA precursors.
- About 30% of the NMOGs from new vehicles could not be speciated (IVOCs), which may contribute to SOA formation.

Gordon et al., 2014, ACP
SOA formation from gasoline vehicles during driving cycle

New European Driving Cycles, NEDC

- SOA Production factor: 0.344-0.347 g kg\(^{-1}\);
- SOA/POA ratios: 9-15;
- Traditional single-ring aromatics and naphthalene can only explain less than 20% of the formed SOA.

Platt et al., 2013, ACP
Large gaps between measured and calculated SOA

- **Idling**: 30-55%
- **Driving**: Less than 1% !!!

Zhang et al., in preparation
Zhao et al., 2016, EST

Predicted SOA formation from gasoline vehicles emissions of IVOC

- Using the chassis dynamometer testing at CARB; UC;
- Measured the emission factor of IVOCs from GVs exhaust;
- Estimated the SOA formation by using published SOA yields based on smog chamber;
- IVOC emissions only correspond to approximately 4% of NMHC, but they are estimated to produce as much or more SOA than single-ring aromatics.
- Even adding IVOC formed SOA, about 30% and 65% of measured SOA remains unexplained.

Zhao et al., 2016, EST
formation of SOA from IVOC?

IVOC-to-NMHCs ratios
- Hot Cycles: 0.17
- Cold UC: 0.04

IVOC-to-POA ratios
- Hot Cycles: 8.5
- Cold UC: 7.3

$$\Delta M = [HC] \times (1 - e^{-k_{OH} [OH] \times \Delta t}) \times \gamma$$
• IVOCs-to-NMHCs ratios: 0.17;
• IVOC SOA contribute: 603-1189% at idling;
• IVOC-SOA contribute 6-130% under driving

Overestimated!
- IVOCs-to-NMHCs ratios: 0.04;
- IVOC SOA contribute: 135-266% at idling;
- IVOC-SOA contribute 2-31% under driving.
• IVOCs-to-POA ratios: 8.5
• IVOC-SOA contribute 1-3% at idling;
• IVOC-SOA contribute 4-22% under driving.
• CARB ratios are not suitable for our cars.

Underestimated!
field observation in China

- One year concurrent observation (2012-2013) 48-h Sampling, biweekly

(Ding et al., *JGR* 2014, 2016; *ACP* 2015; *SR* 2016; *ES&T*, 2017)
SOA tracers analysis

- 13 SOA tracers

Silylation

Methylation

GC-MS

Isoprene

Monoterpenes

β-Caryophyllene & Aromatic hydros.

2-Methylglyceric acid (MGA)

2-Methyl-1,3,4-trihydroxy-1-butenes

2-Methyltetrols

3-Methyl-2,3,4-trihydroxy-1-butene

2-Methyl-1,3,4-trihydroxy-1-butenes

Monoterpenes

β-Caryophyllene & Aromatic hydros.
Tracers of isoprene SOA

- High levels in summer (red) and southern China
- Unexpected increase in winter (yellow)

Ding et al., SR 2016
MEGAN: \[ E_I = EF_I \times C_L \times C_T \]


**Fall-winter**
**Non-biogenic control**

**Spring-summer**
**Biogenic emission control**
Biomass Burning affects seasonal trend of isoprene SOA

- Spring-summer: determined by biogenic emissions
- Fall-winter: highly associated with BB enhancement
Tracers of monoterpene SOA

- High levels in spring-summer (blue & red) and southern China
- Unexpected increase in winter (yellow) at some sites
Large amounts of VOCs and NOx from Biomass Burning

<table>
<thead>
<tr>
<th></th>
<th>Tropical Forest</th>
<th>Savannah</th>
<th>Crop Residue</th>
<th>Pasture Maintenance</th>
<th>Boreal Forest</th>
<th>Temperate Forest</th>
<th>Extratropical Forest</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide (CO₂)</td>
<td>1643 (38)</td>
<td>1686 (38)</td>
<td>1585 (100)</td>
<td>1548 (142)</td>
<td>1489 (121)</td>
<td>1567 (71)</td>
<td>1509 (98)</td>
</tr>
<tr>
<td>Carbon Monoxide (CO)</td>
<td>93 (27)</td>
<td>63 (17)</td>
<td>102 (33)</td>
<td>135 (38)</td>
<td>127 (45)</td>
<td>89 (32)</td>
<td>122 (44)</td>
</tr>
<tr>
<td>Methane (CH₄)</td>
<td>3.07 (1.98)</td>
<td>1.94 (0.83)</td>
<td>5.82 (3.56)</td>
<td>8.71 (4.97)</td>
<td>2.98 (3.14)</td>
<td>3.92 (2.99)</td>
<td>3.98 (3.24)</td>
</tr>
<tr>
<td>Acetylene (C₂H₂)</td>
<td>0.44 (0.35)</td>
<td>0.24 (0.10)</td>
<td>0.27 (0.08)</td>
<td>0.31 (0.29)</td>
<td>0.19 (0.10)</td>
<td>0.29 (0.10)</td>
<td>0.19 (0.09)</td>
</tr>
<tr>
<td>Ethylene (C₂H₄)</td>
<td>1.06 (0.37)</td>
<td>0.82 (0.35)</td>
<td>1.46 (0.59)</td>
<td>1.38 (0.71)</td>
<td>1.42 (0.43)</td>
<td>1.12 (0.35)</td>
<td>1.38 (0.42)</td>
</tr>
<tr>
<td>Ethane (C₂H₆)</td>
<td>1.73 (0.28)</td>
<td>0.65 (0.41)</td>
<td>0.51 (0.49)</td>
<td>0.35 (0.42)</td>
<td>1.70 (1.14)</td>
<td>1.12 (0.87)</td>
<td>1.70 (1.05)</td>
</tr>
<tr>
<td>Propylene (C₃H₆)</td>
<td>0.04 (0.066)</td>
<td>0.012 (0.065)</td>
<td>-</td>
<td>0.002 (0.009)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Propene (C₃H₄)</td>
<td>0.64 (0.43)</td>
<td>0.70 (0.56)</td>
<td>0.68 (0.37)</td>
<td>0.85 (0.66)</td>
<td>1.13 (0.60)</td>
<td>0.95 (0.54)</td>
<td>1.11 (0.61)</td>
</tr>
<tr>
<td>Propane (C₃H₈)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>n-Butane (C₄H₁₀)</td>
<td>0.128 (0.060)</td>
<td>0.10 (0.067)</td>
<td>0.28 (0.13)</td>
<td>0.22 (0.10)</td>
<td>0.41</td>
<td>0.26 (0.11)</td>
<td>0.42 (0.18)</td>
</tr>
<tr>
<td>i-Butane (C₄H₁₀)</td>
<td>0.038 (0.023)</td>
<td>0.016 (0.013)</td>
<td>0.072 (0.036)</td>
<td>0.040 (0.018)</td>
<td>0.12</td>
<td>0.083 (0.10)</td>
<td>0.12 (0.14)</td>
</tr>
<tr>
<td>1-Butene (C₄H₈)</td>
<td>0.11 (0.009)</td>
<td>0.0043 (0.0027)</td>
<td>0.023 (0.013)</td>
<td>0.014 (0.0063)</td>
<td>0.042</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>trans-2-Butene (C₄H₈)</td>
<td>0.17 (0.077)</td>
<td>0.045 (0.022)</td>
<td>0.154 (0.080)</td>
<td>0.15</td>
<td>-</td>
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<td>-</td>
</tr>
<tr>
<td>cis-2-Butene (C₄H₈)</td>
<td>0.11 (0.051)</td>
<td>0.024 (0.051)</td>
<td>0.117 (0.060)</td>
<td>0.11</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1,3-Butadiene (C₄H₆)</td>
<td>0.039</td>
<td>0.052 (0.028)</td>
<td>0.151 (0.072)</td>
<td>-</td>
<td>0.14</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Isoprene (C₅H₈)</td>
<td>0.029 (0.013)</td>
<td>0.011 (0.0055)</td>
<td>0.057 (0.030)</td>
<td>0.050 (0.023)</td>
<td>0.040</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>n-Pentane (C₅H₁₂)</td>
<td>0.024 (0.010)</td>
<td>0.0084 (0.0043)</td>
<td>0.043 (0.023)</td>
<td>0.040 (0.018)</td>
<td>0.030</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2-Methyl-2-Pentene (C₅H₁₀)</td>
<td>8.03 x 10⁻³</td>
<td>0.0352 (0.0032)</td>
<td>0.025 (0.012)</td>
<td>0.056 (0.0025)</td>
<td>0.085</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2-Methyl-1-Pentene (C₅H₁₀)</td>
<td>1.50 x 10⁻³</td>
<td>0.0025 (0.0018)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3-Methyl-1-Pentene (C₅H₁₀)</td>
<td>3.80 x 10⁻³</td>
<td>0.0051 (0.0034)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2-Methyl-2-Pentene (C₅H₁₀)</td>
<td>4.00 x 10⁻³</td>
<td>0.0048 (0.0025)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2-Methyl-1-Pentene (C₅H₁₀)</td>
<td>4.40 x 10⁻³</td>
<td>0.0059 (0.0037)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>Aromatics (C₅H₈)</td>
<td>0.13 (0.056)</td>
<td>0.039 (0.027)</td>
<td>0.36 (0.16)</td>
<td>0.12 (0.055)</td>
<td>0.15</td>
<td>-</td>
<td>0.15</td>
</tr>
<tr>
<td>Cyclopentanone (C₅H₈O)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0016 (0.0012)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2,4-Dimethylpentane (C₇H₁₄)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0086</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2-Methyl-1-Pentene (C₅H₁₂)</td>
<td>2.80 x 10⁻³</td>
<td>0.0035 (0.0021)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>n-Hexane (C₆H₁₄)</td>
<td>0.021</td>
<td>0.013 (0.0074)</td>
<td>-</td>
<td>-</td>
<td>0.055</td>
<td>0.055</td>
<td>0.055</td>
</tr>
<tr>
<td>Hexene (C₆H₁₀)</td>
<td>5.60 x 10⁻³</td>
<td>0.0070 (0.0072)</td>
<td>-</td>
<td>-</td>
<td>0.048</td>
<td>-</td>
<td>0.048</td>
</tr>
<tr>
<td>Pentene (C₅H₁₀)</td>
<td>0.39 (0.16)</td>
<td>0.20 (0.084)</td>
<td>0.15 (0.04)</td>
<td>0.70 (0.32)</td>
<td>1.11</td>
<td>1.11</td>
<td>1.11</td>
</tr>
<tr>
<td>3-Hexene (C₆H₁₀)</td>
<td>0.26 (0.13)</td>
<td>0.080 (0.058)</td>
<td>0.19 (0.06)</td>
<td>0.34 (0.15)</td>
<td>0.48</td>
<td>0.48</td>
<td>0.48</td>
</tr>
<tr>
<td>Xylenes (C₆H₈)</td>
<td>0.11 (0.082)</td>
<td>0.014 (0.024)</td>
<td>0.11 (0.005)</td>
<td>0.11 (0.0030)</td>
<td>0.18</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>Ethylbenzene (C₆H₈)</td>
<td>0.050 (0.036)</td>
<td>0.006 (0.010)</td>
<td>0.067 (0.030)</td>
<td>0.051</td>
<td>-</td>
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</tr>
<tr>
<td>n-Propylbenzene (C₈H₁₀)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.018</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>o-Xylene (C₆H₈)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.64</td>
<td>-</td>
<td>1.64</td>
</tr>
<tr>
<td>m-Xylene (C₆H₈)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.45</td>
<td>-</td>
<td>1.45</td>
</tr>
<tr>
<td>p-Xylene (C₆H₈)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.055</td>
<td>-</td>
<td>0.055</td>
</tr>
<tr>
<td>Ethanol (C₅H₈O₂)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.41</td>
<td>0.16 (0.21)</td>
<td>0.38 (0.35)</td>
</tr>
</tbody>
</table>

(Akagi et al., ACP 2011)
Unexpected high levels of isoprene during non-growing seasons

- Significantly high mixing ratios of isoprene were observed during non-growing seasons from ambient observation results.
- Biomass/biofuel/coal burning might be the potential sources?
Tracer of β-Caryophyllene SOA (SOA$_c$)

- Unexpected high levels in winter (yellow) at many sites in China

(Ding et al., JGR, 2016)
High levels of SOA$_C$ tracer during winter in South China

- Similar seasonal trend at 9 sites in South China
- Highest levels in winter (January)

(Ding et al., in preparation)
Significant impact of Biomass Burning on SOA<sub>C</sub>

- Strong and significant correlations with the BB tracer (levoglucosan)
- BB could be an important source of SOA<sub>C</sub> in wintertime
Biomass Burning could be an important source of SOA.

1. **NOx VOCs** → **OH/O₃/NO₃** → **Oxidation products**
2. **Biomass Burning** → **POA** → **Evolution** → **SOA**
3. **Semi-volatile products**
4. **Homogeneous processes**
5. **Secondary Organic Aerosol**
SOA estimation: Tracer method

\[ f_{soc, hc} = \frac{\sum_i [tr_i]}{[SOC]} \]

(Reindienst et al. 2007)
Spatial distribution of SOA

- High levels of SOA in the southern China;
- Aromatics are dominant over the biogenic VOCs in the northern China;
- The BVOCs’ contributions are high in southern China.
SOA from BVOC?

![Bar chart showing SOA from different sources.

- GEOS-Chem (Fu, 2012)
- RAQMS (Han, 2016)
- WRF-Chem (Jiang, 2012)
- Observation (This study)

Legend:
- Green: isoprene
- Blue: monoterpenes
- Red: sesquiterpenes

(Ding et al., JGR, 2016)
Missing OH Reactivity in a Forest: Evidence for Unknown Reactive Biogenic VOCs

Piero Di Carlo,1,2* William H. Brune,1 Monica Martinez,1† Hartwig Harder,1† Robert Lesher,1 Xinrong Ren,1 Troy Thornberry,3,4† Mary Anne Carroll,3,4 Valerie Young,5 Paul B. Shepson,6 Daniel Riemer,7 Eric Apel,8 Colleen Campbell4

Forest emissions of biogenic volatile organic compounds (BVOCs), such as isoprene and other terpenes, play a role in the production of tropospheric ozone and aerosols. In a northern Michigan forest, the direct measurement of total OH reactivity, which is the inverse of the OH lifetime, was significantly greater than expected. The difference between measured and expected OH reactivity, called the missing OH reactivity, increased with temperature, as did emission rates for terpenes and other BVOCs. These measurements are consistent with the hypothesis that unknown reactive BVOCs, perhaps terpenes, provide the missing OH reactivity.

Carlo et al., 2004, Science
Unexplained SOA at 9 sites in South China

EC method: \[ SOC = OC - \left( \frac{OC}{EC} \right)_p \times EC \]

- SOC \text{Tracer} explains 30-70% of total SOC with an average of ~50%
- SOC \text{Tracer} explains more in summer and fall, less in winter and spring
Summaries

- For important emission sources, including biomass burning and vehicle exhaust, traditional VOCs can explain quite limited portions of SOA formed;
- Further source characterization of these combustion sources and biogenic emission is need with the inclusion of IVOC/OVOC/SVOC to update emission inventories and related emission standards
- Biomass burning could be an important source of traditionally biogenic VOCs and hence contributes to isoprenoid-SOA especially in wintertime.
- Improving SOA monitoring is needed.
- Field observation suggest that SOA reconstructed with SOA-tracer of traditional precursors (including sesquiterpenes) could explain ~50% of SOC estimated by EC-tracer method.
Acknowledgement

- The Strategic Priority Research Program of the CAS.
- NSFC
- MOST
- Students (Bernard F; Liu TY; Mackenzie-Rae F; Deng W; Fang Z; .......)

Thanks for your attention!