Biogenic Secondary Organic Aerosol Tracers in the Pearl River Delta Region

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OUTLINE

➢ Background

➢ Results and discussion

  Levels and composition;
  Influencing factors: Temperature, aerosol acidity

➢ Summary
SOA formation

VOCs \( \xrightarrow{h\nu, NO_x, O_3} \) Oxidation products \( \xrightarrow{} \) Volatile products (gas phase)

Semi-volatile products

Nucleation reactions

Condensation

POA (particle phase) \( \xrightarrow{\text{Evolution}} \) SOA

Secondary Organic Aerosol (SOA)
Impact of SOA

Regional
- Haze
- Fine particle pollution
- Public health

Global
- CCN (cloud condensation nuclei)
  - Cloud properties;
  - Water cycle
- Scattering solar radiation
  - Radioactive forcing

......
Emission of SOA precursors

Global VOC emission: **Biogenic >> Anthropogenic**

Global Biogenic VOC emission

1150 (Tg/yr):

- Isoprene: 503
- Monoterpenes: 127
- ORVOC: 260

Global Anthropogenic VOC emission: 100 (Tg/yr)

(Guenther et al., JGR 1995; Piccot et al., JGR 1992)
Biogenic precursors

Isoprene
myrcene
alpha-pinene
beta-pinene
alpha-thujene
isoprene

Isoprene & Terpinene

limonene
carene
sabinene
camphene
Increase of SOA in the future

(Tsigaridis and Kanakidou AE 2007)
PRD region: High precursor emissions

- **Biogenic**: Subtropics
  - Annual temp. > 20 °C

- **Anthropogenic**: Rapidly developing region; Industrialized & Urbanized; Large populations.

PRD
**PRD region:**
High aerosol acidity

- SO$_2$, NO$_x$ emissions
- SO$_4^{2-}$+NO$_3^-$ $\gg$ NH$_4^+$
- pH: 0.25 (-0.62–2.35)

**Acid-catalyzed reactions**

(Jang et al., Science 2002)

(Chan et al., 2008; Wang et al., 2009; Ding et al., 2009; Pathak et al., 2004)
PRD region:
High levels of oxidants

(Meng et al. Science 1997)

(Wang et al. ACP 2009)
SOC in Hong Kong

Summer

SOA: up to 8.83 ug/m$^3$

**Biogenic** sources dominant

Enhancement when impacted by PRD region

*(Hu et al. JGR. 2008)*
Motivation

- Biogenic SOA tracers in the background of PRD during the worst air pollution period (fall-winter);

- Influence of temperature and aerosol acidity on biogenic SOA tracers
Sampling Information

Wangqingsha (WQS)
2007.10-11
30m rooftop
SOA tracers - isoprene

2-Methyltetrols

2-Methanethreitol

2-Methylerythritol

2-Methylglyceric acid (MGA)

3-Methyl-2,3,4-trihydroxy-1-butene (MTHB)
SOA tracers – α-pinene

Pinic acid
Pinonic acid
3-Hydroxyglutaric acid (HGA)

3-Hydroxy-4,4-dimethylglutaric acid (HDMGA)
3-Methyl-1,2,3-butanetricarboxylic acid (MBTCA)
SOA tracers-sesquiterpene

β-caryophyllene

\[ \beta\text{-caryophyllinic acid} \]

\[ \text{RO}_2 \text{ or HO}_2 \]
Chemical analysis

24-hr PM$_{2.5}$ sample

Extract

Internal standards
Sonication

Diazomethane

BSTFA + 1% TMCS

Methylation

Silylation

GC-MS
Levels and composition

PM$_{2.5}$:
- average 113 µg m$^{-3}$
- highest 171 µg m$^{-3}$

Visibility:
- worst 5.5 km

Isoprene > α-Pinene > Sesquiterpene
Isoprene SOA tracers

Isoprene: 30.8 (5.77-68.3) ng/m$^3$

2-methyltetrols
Influencing factor for isoprene: Temperature

Temperature

Emission & Reactive rates

SOA
Influencing factor for isoprene: Aerosol acidity

\[ [H^+] = 2 \times [SO_4^{2-}] + [NO_3^-] - [NH_4^+] \]

\[ [H^+] : 0.15 \sim 0.77 \ \mu\text{mol/m}^3 \]

Aerosol acidity

Acid-catalyzed reaction

SOA
Influencing factor for isoprene: Aerosol acidity

Isoprene SOA tracers vs. $[\text{H}^+]$

Chamber study $9.25 \times 10^3$ ng C m$^{-3}$ per µmol $[\text{H}^+]$ m$^{-3}$

(Surratt et al., 2007; Offenberg et al., 2009)

Ambient observation $2.62 \times 10^1$ ng C m$^{-3}$ per µmol $[\text{H}^+]$ m$^{-3}$

(This study)

2 orders of magnitude lower!
Implication of acidity effect

**Huge gap** between chamber and ambient in slope

<table>
<thead>
<tr>
<th>Cause</th>
<th>Chamber (Surratt et al., 2007; Offenberg et al., 2009)</th>
<th>Ambient (This study)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH</td>
<td>&lt;30%, dry condition</td>
<td>56% (40 to 83%)</td>
</tr>
<tr>
<td>Isoprene levels</td>
<td>excess amount</td>
<td>emission strength varied</td>
</tr>
<tr>
<td>Acidity</td>
<td>pH measurement</td>
<td>charge balance</td>
</tr>
<tr>
<td>Tracer quantification</td>
<td>cis-ketopinic acid</td>
<td>erythritol……</td>
</tr>
</tbody>
</table>

**Implication**

Chamber results **overestimate** acid-catalyzed isoprene-SOA tracer production in the ambient
α-Pinene SOA tracers

(b)

Concentrations (ng/m$^3$)

α-Pinene: 6.61 (0.91-18.3) ng/m$^3$

pinonic acid
Influencing factor for \( \alpha \)-Pinene: Temperature

No significant correlations with temperature
Influencing factor for \( \alpha \)-Pinene: Aerosol acidity

Reversed trends

great uncertainties would occur when using tracers to infer SOA in ambient

(Offenberg et al. ES&T. 2009)
Influencing factor for α-Pinene: Aerosol acidity

α-Pinene SOA tracers vs. [H⁺]

Chamber study
- 3.8×10³ ng C m⁻³ per µmol [H⁺] m⁻³

(Offenberg et al., 2009)

Ambient observation
- 7.8 ng C m⁻³ per µmol [H⁺] m⁻³

(This study)

2 orders of magnitude!
Sesquiterpene SOA tracers

\[ \text{Concentrations (ng/m}^3) \]

\[ 0.0 \quad 0.5 \quad 1.0 \quad 1.5 \quad 2.0 \quad 2.5 \]

**\( \beta \)-caryophyllinic acid**:

\[ 0.54 \ (0.03-1.97) \text{ ng/m}^3 \]
Influencing factors

No significant correlations with aerosol acidity and temperature
Summary

- **Tracer levels:**
  - Isoprene > Pinene > Sesquiterpene

- **Composition:**
  - 2-Methyltetrols were dominant in isoprene tracers;
  - *cis*-Pinonic acid was dominant in α-pinene tracers.

- **Influencing factors:**
  - Temperature: Significant for isoprene; not so for others
  - Acidity: similar in trend; different in slope
Thank You!