Revisiting the organic aerosol in southeast US

Yiqi Zheng, Jingqiu Mao
University of Alaska Fairbanks

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Coauthors: Joel Thornton (U. Washington), Nga Lee Ng (Georgia Tech), Erin McDuffie (Dalhousie U.), Jose Jimenez (CU Boulder), Eloise Marais (U. Leicester)

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Anthropogenic influence on BSOA formation

GEOS-Chem v12.1.0

ISOP MTP

+OH, O₃ → RO₂ → Gas-phase Products → +HO₂ → +NO

Gas-Aerosol partitioning

Volatility Basis Set (VBS) [Pye et al. 2010]

“A dry”

“Aqueous-phase reactive uptake”

“Wet”

6 ISOP-SOA species [Marais et al. 2016]

NOₓ SO₂

IMPROVE Observation
OA = 2.2 × OC
Jun-Jul-Aug Southeast US

Sulfate: \( k = -0.68 \, \mu g/m^3/yr \)
OA: \( k = -0.18 \, \mu g/m^3/yr \)
Model overestimates the 10-yr OA trend and the ISOP contribution

Units of trend (k): µg/m³/year

GEOS-Chem v12.1.0, 2°×2.5°, SEUS, JJA-average

<table>
<thead>
<tr>
<th>Fraction in total OA (%)</th>
<th>GC v12.1.0</th>
<th>Zhang et al., 2018</th>
<th>Xu et al., 2018</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISOP-SOA</td>
<td>58</td>
<td>13</td>
<td>21-36</td>
</tr>
<tr>
<td>MTP-SOA</td>
<td>22</td>
<td>42</td>
<td>&gt; 19-34</td>
</tr>
</tbody>
</table>
Large month-to-month variation in 2005-2007

IMPROVE OA [µg/m^3]

Model OA (default) [µg/m^3]

Large month-to-month variation due to aerosol acidity \([H^+]\)

**IMPROVE OA** [µg/m³]

- 08
- 07
- 06

**Model OA (default)** [µg/m³]

**ISOP_{emis}** [mg/m²/hr]

- 08
- 07
- 06

**Model SO₄** [µg/m³]

- 08
- 07
- 06

**Model H⁺** [mol/L]

- 08
- 07
- 06
High [H⁺] in Aug 2005-2007 due to insufficient NH₃

- **IMPROVE OA [µg/m³]**
  - 08
  - 07
  - 06

- **ISOP_{emis} [mg/m²/hr]**
  - 08
  - 07
  - 06

- **Model SO₄ [µg/m³]**
  - 08
  - 07
  - 06

- **Model H⁺ [mol/L]**
  - 08
  - 07
  - 06

- **Model OA (default) [µg/m³]**
  - 08
  - 07
  - 06

- **NH₃_{emis} [x10⁸ kg]**
  - 08
  - 07
  - 06
High $[H^+]$ in Aug 2005-2007 due to insufficient NH$_3$

**Model OA (default) [µg/m$^3$]**

**IMPROVE OA [µg/m$^3$]**

\[ r^2 = 0.87 \]

\[ r^2 = 0.26 \]

**IEPOX-SOA vs NH$_3$**

2005-2007 $r^2 = 0.87$ (-)
2008-2014 $r^2 = 0.26$ (-)
Large month-to-month variation in 2005-2007

**IMPROVE OA [µg/m³]**

- 08
- 07
- 06

High aerosol acidity [H⁺] (in an NH₃-limited regime)

**Model OA (default) [µg/m³]**

- 08
- 07
- 06

High IEPOX-SOA

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**Why the model-obs. difference?**

- IEPOX-SOA too sensitive to [H⁺]
- [H⁺] too high
- Overestimate IEPOX-SOA

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**Model Development**

- Coating effect for IEPOX uptake
- Fixed [H⁺]
- Update MTP-chemistry (future work)
Coating: reducing $\gamma_{\text{IEPOX}}$ and $\gamma_{\text{IEPOX}}$ sensitivity to $[\text{H}^+]$

**Model – Default**

$\gamma_{\text{IEPOX}} = \text{Function (H}^+, \ldots\text{)}$

Rate = Function ($\gamma_{\text{IEPOX}}\cdot A_{\text{sulfate}}$)

**Model – Coating**

Fitted based on [Gaston et al., 2014].

$\gamma_{\text{IEPOX}} = \text{Function (H}^+, \ldots\text{)}$

$\gamma_{\text{new}} = \gamma_{\text{IEPOX}} \cdot (1 - 1.3 \cdot \chi_{\text{org}})$

Rate = Function ($\gamma_{\text{new}}\cdot A_{\text{sulfate+org}}$)

Observed $\chi_{\text{org}}$ and assuming $[\text{H}^+] = 0.1 \text{ mol/L}$ (2013 SOAS campaign data)

Modeled $[\text{H}^+]$ and $\chi_{\text{org}}$
Model development: coating effect

Model – Default

\[ \gamma_{IEPOX} = \text{Function} \left( H^+, \ldots \right) \]
\[ \text{Rate} = \text{Function} \left( \gamma_{IEPOX}, A_{\text{sulfate}} \right) \]

Model – Coating

\[ \gamma_{IEPOX} = \text{Function} \left( H^+, \ldots \right) \]
\[ \gamma_{\text{new}} = \gamma_{IEPOX} \times \left( 1 - 1.3 \times \chi_{\text{org}} \right) \]
\[ \text{Rate} = \text{Function} \left( \gamma_{\text{new}}, A_{\text{sulfate+org}} \right) \]

Model – Coating_fixedH

\[ \gamma_{IEPOX} = \text{Function} \left( H^+ = 0.1 \text{ mol/L}, \ldots \right) \]
\[ \gamma_{\text{new}} = \gamma_{IEPOX} \times \left( 1 - 1.3 \times \chi_{\text{org}} \right) \]
\[ \text{Rate} = \text{Function} \left( \gamma_{\text{new}}, A_{\text{sulfate+org}} \right) \]

Trend of acidity

Current model: decrease in acidity
[Weber et al. 2016]: remain unchanged
[Silvern et al. 2017]: increase in acidity
Adding coating effect improves model performance

Month: JJA

Observation:
k = -0.18

Units: µg/m³/year
Adding coating effect improves model performance

Observed OA

Model OA (default)

Model OA (coating)

Model OA (coating_fixedH)
Summary & Future work

- **Coating** effect for IEPOX uptake & fixed [$H^+$] improves model performance.
- Underestimation of MTP-SOA?

Issues to resolve: **Loss of mass**; lack of observational constraint; double counting with VBS. MTP-chemistry will be updated in collaboration with Prof. Sally Ng’s group.
backup
Large month-to-month variation dominated by IEPOX-SOA

**IMPROVE OA [µg/m³]**

**Model OA (default) [µg/m³]**

**IEPOX-SOA [µg/m³]**

**OA – IEPOX-SOA [µg/m³]**

Dominated by IEPOX-SOA
Observed OA show no big difference between Jun-Jul-Aug

**IMPROVE OA [µg/m³]**

- 08
- 07
- 06

**Model OA (default) [µg/m³]**

**Observation**

**IMPROVE OC (µg/m³)**

**EPA-CSN OC (µg/m³)**

**SEARCH OC (µg/m³)**

**EPA-CSN OC-NOISH (µg/m³)**
NH₃ emission

[Paulot et al., 2014]
Modeling vs. Observation $\text{NH}_x$

Modeling:
$\text{NH}_x = \text{NH}_3 + \text{NH}_4$ (ppbv)

Observation (NADP):
$\text{NH}_x$ WetDep Flux ($\times 10^{-5}$ kg/m$^2$)