Global modeling of secondary organic aerosol with an explicit scheme

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Outline

- The effect of iron chemistry on SOA formation in cloud

- Radiative forcing of organic aerosol: effect of SOA and brown carbon (BrC)
Introduction: How are organic aerosols formed?

Semi-Volatiles

Oxidation by OH, O₃, NO₃

Aromatics (e.g., Toulene)

Monoterpenes
Sesquiterpenes

Isoprene

Reversible condensation

Aerosol phase reaction

Cloud Processing

Secondary Organic Aerosol

Primary Organic Aerosol

Direct Emission

Based on Heald C. L. Lecture, 2007
Model description

3-D atmospheric chemical transport model (IMPACT)

- Microphysics of sulfate aerosol and the interactions between sulfate and non-sulfate aerosols (Liu et al., 2005).

- SOA formation from gas-particle partitioning of sVOCs (Lin et al., 2012). For example,

\[ \text{Toulene} \xrightarrow{\text{OH}} \text{CRES} \xrightarrow{\text{OH}} \text{POXY} \xrightarrow{\text{NO}_2} \text{NITP} \xrightarrow{\text{NO}_3} \text{R4N2} \]

- Gas-particle partitioning

- Formation of SOA from reaction of glyoxal and methylglyoxal in cloud droplets and aqueous aerosols (Lin et al., 2013).

- Formation of non-evaporative SOA from epoxides (Lin et al., 2012).
Multiphase reaction scheme to simulate SOA formed in cloud

Representing all processes explicitly:

\[
\frac{dC_{aq}}{dt} = R_{aq} + \frac{k_t}{RT} \cdot P_g - \frac{k_t}{HRT} Q \cdot C_{aq}
\]

- \(k_t\): gas transfer coefficient
- \(P_g\): gas phase partial pressure
- \(Q\): aqueous phase diffusion rate limitation factor

Oxalic acid is a major component of SOA formed in cloud

isoprene, benzene, toluene

glyoxal, methylglyoxal, OH

organic acids (glyoxylic acid, oxalic acid, pyruvic acid)

SOA
Iron (Fe) chemistry in cloud

- Contribute to the budget of OH radicals in cloud

\[
\begin{align*}
[\text{Fe(OH)}]^2+ + h\nu & \rightarrow \text{OH} + \text{Fe}^{2+} & \text{(R1)} \\
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{OH} + \text{Fe}^{3+} + \text{OH}^- & \text{(R2)} \\
\text{Fe}^{2+} + \text{OH} & \rightarrow [\text{Fe(OH)}]^2+ & \text{(R3)}
\end{align*}
\]

- A sink of oxalic acid (H\(_2\)C\(_2\)O\(_4\))/oxalate (C\(_2\)O\(_4\)^{2-}\))

\[
\text{Fe (C}_2\text{O}_4)^{3-2n} + h\nu \rightarrow \text{Fe}^{2+} + (n-1) \text{C}_2\text{O}_4^{2-} + \text{CO}_2 + \text{CO}_2^- (n=1,2,3)
\]

But no global SOA models has included iron chemistry.

We assumed 3.5% mass of dust aerosol composed of Fe (Taylor and McLennan, 1985), only 5% of which could be dissolved into cloud water (Ito and Xu., 2013).
Predicted global budget of aqueous OH radical

Globally, iron chemistry contribute over 50% of aqueous OH radical sources and over 20% of sinks.
Iron chemistry increases the in-cloud OH radical

The ratio of annual mean in-cloud OH radical source in simulation with Fe chemistry to that in simulation without Fe chemistry.

Annual mean aqueous OH concentration at 971 hPa (units: mol/L) Values are on a logarithmic scale.
Dissolved iron chemistry decreases oxalic acid/oxalate

Annual mean oxalate concentration at 971 hPa

Global change in oxalate reaction rates (Tg/yr)

<table>
<thead>
<tr>
<th></th>
<th>Chemical production</th>
<th>Chemical destruction</th>
<th>Net production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulation without Fe chemistry</td>
<td>22.9</td>
<td>7.2</td>
<td>15.7</td>
</tr>
<tr>
<td>Simulation with Fe chemistry</td>
<td>32.2</td>
<td>27.8</td>
<td>4.4</td>
</tr>
</tbody>
</table>
Radiative forcing of OA: effect of SOA and brown carbon
Motivation

- Very few global model SOA forcing estimates exist, although SOA is an important component of aerosol.

- The contribution of BrC absorption to total aerosol absorption could be significant. However, most of existing global models assume OA to be almost purely scattering.
Imaginary part of refractive index for POA BrC

![Graph showing the imaginary part of refractive index as a function of wavelength (λ) for POA BrC. The graph includes data from Kirchstetter et al. (2004), Chen and Bond (2010), and other literature.]
We use Kirchstetter et al. (2004) and Chen and Bond (2010) as potential limits of the light-absorbing properties of BrC.
# Simulation set up

<table>
<thead>
<tr>
<th></th>
<th>H-ABS (high-absorbing case)</th>
<th>L-ABS (low-absorbing case)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High refractive index</td>
<td></td>
<td>Low refractive index</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biomass burning POA</td>
<td>100% are BrC</td>
<td>only biofuel and residential coal burning POA can absorb sunlight</td>
</tr>
<tr>
<td>Fossil fuel/biofuel POA</td>
<td>only biofuel and residential coal burning POA can absorb sunlight</td>
<td></td>
</tr>
<tr>
<td>SOA</td>
<td>The same size distribution and BrC fraction as biomass burning POA</td>
<td>The same size distribution and BrC fraction as fossil fuel/biofuel POA</td>
</tr>
</tbody>
</table>
Direct radiative forcing of total OA (SOA+ POA)

BrC absorption: 14%~57% of BC absorption predicted in the model
Compare range of forcing to that estimated by others

- SOA
- POA
- tOA (SOA + POA)

Radiative forcing (W m\(^{-2}\))

- This work
- Other models
- Aerocom Phase I models
- Other models

Based on SOA constrained by AMS measurements (Spracklen et al. 2011)
Conclusion

- The inclusion of iron chemistry increases the aqueous OH radicals and decreases the oxalate concentration.
- The radiative forcing of SOA is predicted to range from -0.12 to -0.34 W m\(^{-2}\).
- BrC leads to an atmospheric absorption of from 0.13 to 0.52 W m\(^{-2}\).
- A large uncertainty of OA forcing associated with BrC and SOA.
Sources of brown carbon

Biomass and biofuel burning (Kirschstetter et al., 2004; Chen and Bond, 2010; Saleh et al., 2013).

Residential coal burning (Bond et al., 1999; Arola et al., 2011)

Formed in heterogeneous reactions from dienes (Limbeck et al., 2003)

generated from the photooxidation of α-pinene and toluene in the presence of NOx (Jaoui et al., 2008)

Formed from the aqueous phase reactions involving glyoxal and methyglyoxal (Shapiro et al., 2009).

Other mechanisms
Comparison of Oxalate and OH

OH radicals in remote continental clouds

Arakaki et al.(2013)
North America
Measured average: 7.2E-15 mol/L

Simulation
With Fe chemistry: 7.5E-14
No Fe chemistry: 7.4E-14
# Global mean AAOD at 550 nm

<table>
<thead>
<tr>
<th>Author</th>
<th>BC AAOD</th>
<th>OM AAOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chung et al. (2012)</td>
<td>0.0077 (0.006 ~ 0.009)</td>
<td>0.0018 (0.001 ~ 0.003)</td>
</tr>
<tr>
<td>Bond et al. (2013)</td>
<td>0.00605</td>
<td></td>
</tr>
<tr>
<td>This work</td>
<td>BC+OM AAOD 0.003000 (H-ABS)</td>
<td>BC+OM AAOD 0.00224 0(L-ABS)</td>
</tr>
</tbody>
</table>
SOA from gas-particle partitioning

- Basic photochemistry of O$_3$, OH, NOx and VOCs (Ito et al., 2007)
- Epoxide formation from isoprene (Paulot et al., 2009)
- HO$_x$ regeneration through isoprene oxidation proposed by Peeters et al. (2009) but with a recycled rate reduced by a factor of 10.

Select species that form SOA based on criteria from Griffin et al. (2002).