Advances in understanding and modeling climate effects of organic aerosols

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  Ryan Sullivan, Lorena Miñambres, Taehyoung Lee, Amy Sullivan, and
  Gavin McMeeking

- Yinon Rudich

.. And disclaimer / apologies
Atmospheric Organic Aerosol

- **Challenge:** Understand and quantify organic aerosols’ life cycle and their atmospheric, climate and health-related processes

- **Problem 1:** What is the atmospheric loading?
  - And composition (affects everything)

- **Problem 2:** What is the budget that results in that loading?
  - Primary (?) emissions
  - Secondary sources
  - Removal processes
  → These in turn control the composition!

- **Problem 3:** What sizes of particles does the OA end up in and what are their mixing states with inorganic components?
  - affects everything: optical properties, cloud impacts, removal rates, …

ACE-Asia (2001): 3 groups measured high OA off Asia. GEOS-Chem simulation factor of 10-100 too low [Heald et al., 2005]

Models drastically underestimate SOA from 4 campaigns [Volkamer et al., 2006]

Goldstein and Galbally [2007] suggest that SOA source may be anywhere from 140-910 TgC/yr.

Room for everyone’s favourite source/process in models that are woefully inadequate.
THE MODELING CHALLENGE: BOTTOM-UP VS. TOP-DOWN

Aqueous SOA formation
[Lim et al., 2005; Carlton et al., 2006; Sorooshian et al., 2007; Volkamer et al., 2007]

New precursors
[Kroll et al., 2005; Lim and Ziemann, 2009; Volkamer et al., 2009]

OH Recycling
[Lelieveld et al., 2008]

PBAP
[Jaenicke et al., 2005; Heald and Spracklen, 2009; Burrows et al., 2009]

Dynamic volatility
[Donahue et al., 2005]

SV-POA & IVOCs
[Robinson et al., 2007]

SOA Yields = f(RH, NOx, acidity..)
[Inua et al., 2004; Ng et al., 2007; Surratt et al., 2007]

NPF
[Martin et al., 2010; Vakkari et al., 2011; Smith et al., 2008; Boy et al., 2008]

What about sinks??

OA has MORE SOURCES and is MORE DYNAMIC than understood in 2005.

Too many (underconstrained) processes...
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Try one top-down approach...
IF ONLY AEROSOL IN THE ATMOSPHERE WAS OA, WHAT LOADING IS IMPLIED BY SATELLITE AOD?

Calculate the “hypothetical” AOD implied by a constant 1 µg/sm³ profile over the land, and see how we need to scale this locally to make up ENTIRE AOD reported by MISR.

Inverted OA loading is 3.5 TgC over land. Assume a 6 days lifetime = 215 TgC/yr → extrapolate to include outflow ~430 TgC/yr. (middle of Goldstein & Galbally)

Slide courtesy Colette Heald
This is more than THREE TIMES what is currently included in global models....

BUT at the low end of Goldstein & Gallbally [2007] range.

Also in relatively good agreement with Spracklen et al. [2011] estimate.

After removing dust, checking other assumptions.
Target: OA source is likely in the 100-150 TgC/yr range

Current global model source is about ½ of this. And largest discrepancies with observations are in anthropogenic source regions.

Marine OA and continental PBAP do not appear to be dominant contributors to global fine PM [Lapina et al., 2011; Heald and Spracklen, 2009]

Fragmentation may be an important sink of OA (will allow us to add more sources without filling up the atmosphere)

PRIORITY: aqueous-phase SOA and constraints on OA deposition
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PrioritY: aqueous-phase SOA and constraints on OA deposition

* But remember mass isn't everything
"Real-time" heterogeneous ice nuclei measurement (~1 – 100 L⁻¹ !!)

Summary of IN composition (isolated using the CSU CFDC) based on TEM elemental compositions (several studies)

Definitely not all “soot”
Some are biological (PBAP)
What else???

Dust and metal oxides (20-80%)

Carbonaceous (0-60%)

Mode size (independent of composition) ~ 0.5 microns

Slide courtesy Paul DeMott
Fires are an IN source, although fresh biomass burning particles by total number are inefficient IN.

\[ T_{\text{CFDC}} = -30 \, ^\circ\text{C} \]

1-5 min averages

Slide courtesy Paul DeMott
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PRIORITY: aqueous-phase SOA and constraints on OA deposition

Seek ways to link evolving composition to key aerosol properties

Slide courtesy Colette Heald
Our focus:
Understand controls on OA hygroscopicity → help inform evolving understanding of OA sources and atmospheric evolution

<table>
<thead>
<tr>
<th>By mass/source</th>
<th>By age/oxidation state</th>
<th>By molecular structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>direct emissions</td>
<td>physical age, photochemical age</td>
<td>explicit speciation</td>
</tr>
<tr>
<td>product schemes</td>
<td>principle components HOA/OOA/LV-OOA ...</td>
<td>functional group composition</td>
</tr>
<tr>
<td>volatility basis set</td>
<td>O:C and H:C ratio</td>
<td>master chemical mechanism</td>
</tr>
<tr>
<td>approach</td>
<td></td>
<td>explicit oxidation state</td>
</tr>
</tbody>
</table>

Increasing level of scientific understanding
Increasing complexity, increasing uncertainty
Motivation: 0.4 W m$^{-2}$ in indirect forcing

How important is organic aerosol hygroscopicity to aerosol indirect forcing?

Xiaohong Liu$^{1,3}$ and Jian Wang$^2$

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“The simulation results show that the uncertainty in organics aerosol hygroscopicity, based on current understanding and our model formulation, may lead to an uncertainty of about 0.4 W m$^{-2}$ ... . This uncertainty is comparable to or even larger than those due to autoconversion parameterization and tuning parameters related to entrainment, drizzle and snow formation.”
CCN activity: the $\kappa$ grid

Grid derived assuming solutions ~obey Raoult’s Law (water activity ~scales with mole fraction) * Fixed surface tension *

$\kappa$ range: $0 - 1$

$\kappa$ for NaCl: $1.2$

$\kappa$ for $(\text{NH}_4)\text{SO}_4$: $0.6$

Best fit $\kappa$: $0.07$

[Petters and Kreidenweis, 2007; 2008 ACP]
Organic aerosol species: Factors that determine apparent $\kappa$

- Hygroscopicity
- Solubility / phase
- Surface tension

What range in apparent $\kappa$ should we expect for organic species?

- If truly insoluble, or deliquescence-limited, $\kappa \sim 0$
- Otherwise, for aqueous solution behavior that approximates Raoult’s Law, we expect $\kappa$ to be inversely related to organic species molar volume
\[ \kappa = \frac{\text{molar volume of water}}{\text{molar volume of solute}} = \frac{MW_w}{\rho_w} \frac{\rho_s}{MW_s} \]

Expect a negative linear relationship in log-log space.
Variation of $\kappa$ with $M_{\text{W}_{\text{org}}}$

- ammonium oxalate monohydrate (0.24 - 0.48)
- oxalic acid dihydrate (0.27 - 0.36)
- levoglucosan (0.2)

Raoult’s law appears valid up to molar volumes ~200 +/- factor of 2, due to experimental uncertainties, dissociation, solution nonidealities, surfactant properties.

[Petters et al., GRL, 2009]
For large molecules, revised expectations....

(soluble “polymers” are more hygroscopic than would be expected for their size)

(Flory-Huggins)

(Raoult’s law)

Apparent hygroscopicity [-]

Molar volume [cm$^3$ mole$^{-1}$]
Compiled data (single compounds)

- Pinic acid: 0.16 – 0.42
- SR fulvic acid: 0.057 – 0.077
- Polyethylene glycol: 0.036 – 0.059

[Petters et al., GRL, 2009]
Compiled data (single compounds)

We haven’t plotted anything “insoluble” here

[Petters et al., GRL, 2009]
With solubility limits

Composition of saturated solution: \( \frac{\text{volume of solute}}{\text{volume of water}} \)

- **Flory-Huggins**
- **Raoult's law**

Solubility limited

Apparent hygroscopicity [-]

Molar volume [cm\(^3\) mole\(^{-1}\)]
Summary of role of molecular size

Smallest molecules bounded by $\kappa \sim 0.5$ (MAX)
$\kappa \sim 0.3$ probably more reasonable

Expect $\kappa \sim 0.05$ for large, soluble molecules

May observe $\kappa \sim 0$ for many sizes of molecule

[Petters et al., GRL, 2009]
… but functional groups matter too

Strongly tied to optical properties as well

Flory-Huggins

Need to be highly functionalized to be large and soluble

[Petters et al., GRL, 2009]
What do observations indicate?
Smoke from biomass burning

bimodal hygroscopicity distributions

(Carrico et al., ACP, 2010)
Smoke from biomass burning

- Less-hygroscopic, organic-dominated mode, $\kappa \sim 0.05 - 0.2$
- Co-emitted salts dominate more-hygroscopic mode
- Bimodal hygroscopicity distributions

(Carrico et al., ACP, 2010)
Atmospheric observations

Gunthe et al., *ACP*, 2009 (Amazonia)

Estimated $\kappa_{\text{org}} \sim 0.1$ for “biogenic SOA from the tropical rainforest of Amazonia”

CSU (Manitou Forest, CO)

Overall $\kappa \sim 0.15$ for biogenically-dominated aerosol in the CO Rocky Mountains
Atmospheric observations (cont’d)

Chang et al., ACP, 2010
(rural Ontario)
estimated $\kappa_{org} \sim 0.05 – 0.22$;
$\kappa_{org} \sim 0$ for unoxidized component
$\kappa_{org} \sim 0.22$ for oxidized component

And further, suggested that
$\kappa_{org} = 0.29 + 0.05 \cdot O:C$
(for $0.3 < O:C < 0.6$)
Complex mixtures: lab-generated SOA

κ ~ 0.1

Lab α-pinene SOA:
Engelhart et al., ACP, 2008: 0.11 – 0.14
King et al., GRL, 2007: 0.12
Duplissy et al., GRL, 2008: 0.09 - 0.12
George & Abbatt, ACP, 2010: 0.08 – 0.16

[PRENNI ET AL., JGR, 2007]
Atmospheric “aging” (adding functional groups \( \rightarrow \) increase \( \kappa \)?)

\( \kappa \sim 0.10 \rightarrow \kappa \sim 0.17 \)

(after \( \sim \)2 weeks of oxidation)

\((\alpha\text{-pinene} + O_3 \text{ SOA})\)

Atmospheric “aging” (adding functional groups $\rightarrow$ increase $\kappa$?)

**Model “primary” aerosol**

$k \sim 0 \rightarrow k \sim 0.01$

(after ~week of oxidation)

$k \sim 0 \rightarrow k \sim 0.04 - 0.08$

(George et al., *AtmEnv*, 2009)

$k \sim 0.12 \rightarrow k \sim 0.3$

(after heavy oxidation)

Petters et al., *GRL*, 2006

Massoli et al., *GRL*, 2010
Atmospheric “aging”
(adding functional groups $\rightarrow$ increase $\kappa$?)

$\kappa \sim 0 \rightarrow \kappa \sim 0.01$
(after $\sim$week of oxidation)

$\kappa \sim 0 \rightarrow \kappa \sim 0.04 - 0.08$
(George et al., AtmEnv, 2009)

$\kappa \sim 0.12 \rightarrow \kappa \sim 0.3$
(after heavy oxidation)

Massoli et al., GRL, 2010

heterogeneous reactions
κ relation to ratio O:C

Jimenez et al., Science, 2009
Same axes, for individual compounds:

- Pinic acid
Same axes, for individual compounds:

Atmospheric organic aerosols must be a mixture of low / high $\kappa$ compounds

Not clear why O:C should be predictive of the overall $\kappa_{org}$
OA – composition – κ links: experimental smog chamber approach

C₅ – C₁₇ precursors

[ SOA from precursors ≥ C₁₅ is mostly CCN inactive ]

Linear alkanes and alkenes
Cycloalkanes and -alkenes
Branched compounds

Can predict the number and type of functional groups for many of these systems
Ozone chemistry with cyclic alkenes, linear alkenes, and monoterpenes

Precursor carbon number
Ozone chemistry with cyclic alkenes, linear alkenes, and monoterpenes

Up to C_{10} precursors 0.05 < \kappa < 0.2 is a good constraint
Ozone chemistry with cyclic alkenes, linear alkenes, and monoterpenes

Up to C_{10} precursors $0.05 < \kappa < 0.2$ is a good constraint

At larger carbon number $\kappa$ trends point to solubility limitations
Linking OA component structure to $\kappa$

Approach: create SOA in smog chamber, choosing precursor with a known reaction mechanism

precursor + oxidant = aerosol
Linking OA component structure to $\kappa$

Approach: create SOA in smog chamber, choosing precursor with a known reaction mechanism

precursor + oxidant = aerosol

Slides courtesy of Sarah Suda
Distribution of $\kappa$ in model SOA

e.g., 1-decene + O$_3$ dark reaction, in UCR smog chamber; known reaction mechanism

Collect aerosol on filter → extract → HPLC (separated via gradient elution method using a water/acetonitrile mixture ramped linearly from 0.95/0.05 to 0/100) → atomizer

Fast-scan CCNc

Graph showing particles [cm$^{-3}$] vs. retention time [min].

- more polar
- less polar

decreasing polarity, $\kappa^2$
1-decene + O₃

Tobias and Ziemann, 2001

1-decene

CH₃(CH₂)₇—C=O

C₉ aldehyde

CH₃(CH₂)₇—C=C(CH₂)₇CH₃

C₁₈ secondary ozonide

C₉ biradical

CH₃(CH₂)₇—C=O

C₁ aldehyde

C₉ hydroxy-hydroperoxide

C₁₈ peroxy hemiacetal

H₂O
1-decene + O$_3$

Main aerosol products

- $C_{18}$ secondary ozonide
- $C_{18}$ peroxy hemiacetal
- $C_9$ hydroxy-hydroperoxide

molecule size

oxygen : carbon ratio
1-decene + $O_3$

Main aerosol products

molecule size

$\text{CH}_3(\text{CH}_2)_7-C-O-\text{(CH}_2)_7\text{CH}_3$

$\text{CH}_3(\text{CH}_2)_7=\text{C}=\text{C}=\text{(CH}_2)_7\text{CH}_3$

$\text{O}-\text{O}-\text{H}$

$\text{O}-\text{H}$
Aerosol formed at higher relative humidity should have a higher overall \[
\kappa = \sum \varepsilon_i K_i
\] 
(volume-weighted average)

C\(_{18}\) products dominate

C\(_9\) products dominate

increasing fraction of C\(_9\) products

relative humidity during reaction
Aerosol from 1-decene + O$_3$

($\kappa$ measured directly on total chamber aerosol during expt)

Dry reaction: $\kappa \sim 0.01$

High RH: $\kappa \sim 0.09$
High performance liquid chromatography

compounds sorted by polarity

more polar

less polar

Particles [cm$^{-3}$]

Retention time [min]
High performance liquid chromatography

compounds sorted by polarity

more polar               less polar

Retention time [ min ]

Particles [ cm$^{-3}$]

$k [-]$

$10^3$

$10^2$

$10^1$

$10$

$1$

$0.2$

$0.1$

$0.01$

$0.001$

$0.0001$

$0.00001$
Kappa frequency distribution

Low relative humidity

High relative humidity
Reconstructed overall aerosol $\kappa$-value
κ distributions in model SOA

Overall κ ranges ~0.04 – 0.22
Reconstructed from distributions ≈ directly measured for bulk aerosol
Functional group analysis: Reaction of oleic acid particles with nitrate radicals

![Functional group analysis diagram](image)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Functional group (FG)</th>
<th>MW</th>
<th>μMole FG/ mg aerosol</th>
<th>g FG/ g aerosol</th>
<th>Mole fraction ($X_f$)</th>
<th>FG/ molecule</th>
<th>Mass FG/ molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oleic acid + NO₃</td>
<td>C(O)OH</td>
<td>45</td>
<td>2.75</td>
<td>0.1238</td>
<td>0.055</td>
<td>0.99</td>
<td>44.2</td>
</tr>
<tr>
<td></td>
<td>CHONO₂</td>
<td>75</td>
<td>2.83</td>
<td>0.2119</td>
<td>0.056</td>
<td>1.01</td>
<td>75.7</td>
</tr>
<tr>
<td></td>
<td>C=O</td>
<td>28</td>
<td>1.68</td>
<td>0.0470</td>
<td>0.033</td>
<td>0.59</td>
<td>16.8</td>
</tr>
<tr>
<td></td>
<td>CHOH</td>
<td>30</td>
<td>0.84</td>
<td>0.0235</td>
<td>0.017</td>
<td>0.31</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>CH₂</td>
<td>14</td>
<td>42.28</td>
<td>0.5919</td>
<td>0.839</td>
<td>15.10</td>
<td>211.5</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>50.38</td>
<td>1.00</td>
<td>1.00</td>
<td>18.00</td>
<td>357.2</td>
</tr>
</tbody>
</table>

**Elemental composition**

<table>
<thead>
<tr>
<th>FG</th>
<th>O/C</th>
<th>H/C</th>
<th>N/C (C/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FG</td>
<td>0.35</td>
<td>1.8</td>
<td>0.060 (16.6)</td>
</tr>
<tr>
<td>Combustion EA analyzer</td>
<td>0.39</td>
<td>2.1</td>
<td>0.056 (17.8)</td>
</tr>
</tbody>
</table>
Functional group analysis:
Reaction of oleic acid particles with nitrate radicals

Can see how we arrived at a particular O:C and how FGs relate to $\kappa$
Envisioned parameterization

CCN activity ($\kappa$) = $f$ (molar volume, # carbons, [structure of carbons?], # and type of functional groups, [location of FGs?])
Envisioned parameterization

CCN activity ($\kappa$) =

\[ f(\text{molar volume, \# carbons, [structure of carbons?], \# and type of functional groups, [location of FGs?]}) \]

Optical properties
Volatility
Phase in atmosphere
\( (\text{solid vs. liquid vs. gas; aqueous vs. organic}) \)
Oxidation state
O:O, H:C, N:C
Summary

- The observed range in $\kappa_{org}$ is generally $0 < \kappa_{org} < 0.3$
  - Largest $\kappa_{org}$ is for low MW compounds (e.g., diacids)
  - Exceptions to high MW, low-$\kappa_{org}$ trend are highly functionalized “polymers”
  - Adding functional groups increases $\kappa_{org}$ (e.g., $0.05 \rightarrow 0.1 \rightarrow 0.16$)
    - Liu and Wang (2010) found that $\Delta \kappa$ for SOA of $\pm 50\%$ (from 0.14 to 0.07 and 0.21) changes the CCN concentration 40%
  - Solubility limitations cause decreases of $\kappa_{org} \rightarrow 0$
    (But may be difficult to observe limited-solubility in atmosphere)
- Some closure studies find $\kappa_{org} \sim 0$, especially under anthropogenic influence
  - But many aerosol mixtures could fall into this classification (can be hard to distinguish from $\kappa \sim 0.001$ or even 0.01)
- Often observe overall $\kappa_{org} \sim 0.1$ in field locations
  - We know organic aerosol is a mixture of many compounds
  - In the lab, we now have observed this reflected as a mixture of individual $\kappa_{org}$
  - In our model systems, we can control length of carbon backbone and functionality and thereby link structure with $\kappa$

New analytical techniques will help confirm and extend to ambient aerosol
Implications for (warm) cloud formation

- Cloud albedo controls (e.g., Leaitch et al., 2010):
  - If organic material is internally mixed with sulfate or other high-$\kappa$ compounds:
    - and the organic is $<75\%$ of the mass, then exact composition does not matter too much for total CCN estimates
    - If organic species dominate, then variations in $\kappa_{\text{org}}$ more important
  - **Mixing** state tends to be an important variable that emphasizes $\kappa_{\text{org}}$

- Variations in $\kappa_{\text{org}}$ and in the distribution of $\kappa$ values comprising $\kappa_{\text{org}}$ can provide insights into the sources of atmospheric organic aerosol matter
  - Unequivocally important in establishing the **ambient size distribution**, a primary control on CCN concentrations
Thank you for your attention