How Important Are Organics in Climate Models?

(Are we ready to deal with them?)

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Mary Gilles, Satish Myneni, Steve Maria
NCAR RAF, LBL ALS
How Important Are Organics in Climate Models?

- **The Measurement Perspective**
  - Carbons
  - Bonds
  - Fragments
  - Molecules

- **The Properties**
  - Hygroscopicity
  - Scattering and Absorption
  - Reactions

- **The Climate Burden**
  - Chung and Seinfeld, 2002
  - Maria et al., 2003
Figure 3. Schematic Presentation of Reactions in Polluted Air Leading to Smog Symptoms

Haagen-Smit, 1952
Organic Particle Sources

- combustion
- incineration
- road dust
- power plants
- automobiles
- sea salt
- biogenic
What organics are in particles?

Less than 20% of measured ambient organics can be chemically identified (Rogge et al., 1993; Yu et al., 2001)

Hildemann et al., 1987
Why Measuring Organics Is Difficult

- Concentration in Air:
  - $0.1-20 \mu g \text{ m}^{-3}$
- Particle Mass in Stadium:
  - $1 \text{ g in } 2 \times 10^5 \text{ m}^3$

- Many Different Compounds
Measuring Organic Particles

Total Organic Carbon

Organic Compounds

EGA (Evolved Gas)

GCMS (Chromatography and Mass Spec)
Chemical Building Blocks

Total Organic Carbon

Bonds

Fragments

Organic Compounds

- C-CH,
- C=O, -CS, 
- C=CH, -CH₂, 
- CNH₂, -COH

EGA (Evolved Gas)

AMS, ATOFMS, FTIR, NEXAFS

GCMS (Chromatography and Mass Spec)

C₈H₁₀, C₁₆H₃₂, ..., CₙHₘ
C₃H₄O₄, C₄H₈O₂, ..., CₙHₘOₙ
C₈H₆O₂S₂, C₈H₆O₄S₂, ..., CₙHₘOₙSₗ
C₈H₁₀O₂N₂, C₁₂H₈O₂N₂, ..., CₙHₘOₙNₗ
### Organic Analysis Techniques

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Related Works</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Molecules</strong></td>
<td></td>
</tr>
<tr>
<td>Gas Chromatography MS</td>
<td>Hildemann et al., 1989</td>
</tr>
<tr>
<td>Liquid Chromatography MS</td>
<td>Odum et al., 2000</td>
</tr>
<tr>
<td>Ion Chromatography</td>
<td>Mochida et al., 2003</td>
</tr>
<tr>
<td><strong>Fragments</strong></td>
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<tr>
<td>Aerosol Time-of-Flight MS</td>
<td>Kalberer et al., 2004</td>
</tr>
<tr>
<td>2-Step Laser D/I MS</td>
<td>Morrical et al., 1998</td>
</tr>
<tr>
<td>Time-of-Flight 2° Ion MS</td>
<td>Guazzotti et al., 2003</td>
</tr>
<tr>
<td>EI Time-of-Flight MS</td>
<td>Tervahattu et al., 2002</td>
</tr>
<tr>
<td>Electrospray MS</td>
<td>Bahreini et al., 2003</td>
</tr>
<tr>
<td><strong>Bonds</strong></td>
<td>Krivacsy et al., 2000</td>
</tr>
<tr>
<td>Proton NMR Spectroscopy</td>
<td></td>
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<tr>
<td>Infrared Spectroscopy</td>
<td>Decesari et al., 2000</td>
</tr>
<tr>
<td>NEXAFS/STX Microscopy</td>
<td>Maria et al., 2003</td>
</tr>
<tr>
<td><strong>Carbons</strong></td>
<td>Russell et al., 2002</td>
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<tr>
<td>Evolved Gas Analysis</td>
<td></td>
</tr>
<tr>
<td>TE and ETE Microscopy</td>
<td>Turpin et al., 1990</td>
</tr>
<tr>
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<td>Husar and Shu, 1975</td>
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</tbody>
</table>

Plus: Isotopes, …
Figure 3. FTIR OC concentrations compared to TOT OC measurements, with the 1:1 line shown as a dotted line. Solid circles indicate samples that were collected simultaneously. Open circles represent all other samples collected. The best fit lines (solid) are shown for (a) samples less than 20 minutes in length (slope = 0.91, $R^2 = 0.93$) and (b) all simultaneous samples (slope = 0.90, $R^2 = 0.82$).

Maria et al., 2003
Organic Mass from OC ±70%

Mean is 1.4
- Majority less than 1.4
- Minority at 2.3

Two types of organics
- More hygroscopic (2.3 ± 0.1)
- Less hygroscopic (1.3 ± 0.2)

Russell, 2003
• Asian emissions contain more OC per unit of CO than ground-based measurements in the US and Japan
Figure 3. Individual sidestream cigarette smoke particles. (A) Obtained with a single Nd:YAG pulse (266 nm) at a power density of $1.7 \times 10^7$ W/cm$^2$. Note that most of the organic carbon is present as low mass fragments. (B) Using L2MS with a 600 ns delay between desorption and ionization. Power densities of $1.5 \times 10^7$ W/cm$^2$ for CO$_2$ laser (10.6 $\mu$m) and $4.34 \times 10^6$ W/cm$^2$ for Nd:YAG (266 nm) laser. Mass peaks not labeled are believed to be alkylated-PAH or heterocyclic compounds.

Figure 4. PAH skeletons corresponding to the mass-to-charge of peaks detected in Figures 3B and 5B using the L2MS experiment.
Fragments

Figure 12. Average mass distribution for species with fragments at \( m/z = 44 \) amu during Twin Otter RF17 (37 m (00:47–1:35 UTC), 156 m (2:11–3:11 UTC), and 843 m (3:33–4:20 UTC)).

Bahreini et al., 2003
## Properties of Organic Compounds

<table>
<thead>
<tr>
<th>Organic Groups</th>
<th>Acid</th>
<th>Carbonyl</th>
<th>Alcohol</th>
<th>Alkene</th>
<th>Alkane</th>
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<tr>
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</tr>
</tbody>
</table>

- **Number of Carbons**: Low (C-H) → High (C-H)
- **Number of Oxygens**: High (C=O) → Low (C=O)

Examples:
- Low C-H: Acetic acid, propanoic acid
- High C-H: Palmitic acid, stearic acid
- Low C=O: Ethylene oxide, dioxyethylene
- High C=O: Butyric acid, oxalic acid
Properties of Organic Compounds

- **Acid**
- **Carbonyl**
- **Alcohol**
- **Alkene**
- **Alkane**

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<tr>
<td></td>
<td>O</td>
<td></td>
<td>OH</td>
<td></td>
<td>C</td>
</tr>
</tbody>
</table>

**Number of Carbons**
- high C-H
- low C-H

**Number of Oxygens**
- high C=O
- low C=O

More Oxygen, More Polar

- Likes: Water More
- Uses: More color

More Oxygens, More Color
Climate Implications

Complex Particle Chemistry: Mixed or separated?
Bonds

Total
C=C Alkane
C=O Carbonyl
C=O Acid
C=C Alkene
C-N Amide

Maria et al., unpublished
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Organics Control Water Uptake

Solar radiation

↑RH

less scattering
LESS COOLING

more scattering
MORE COOLING
Organic Aerosol Effects

Indirect Effects

Direct Effect

Reactivity
Hygroscopicity
Wetting
Surface Tension
Absorption
Mixing State
Hygroscopicity and Surface Tension

NO: No solubility or surface tension

↑ CCN (surface tension)

↑ CCN (solubility)

OS: Only Solubility

↑ CCN (surface tension and solubility)

ST: Solubility and surface tension

Ming and Russell, 2004
Organic Role in Fogs and Clouds

- **CCN Chemical Composition**
  - 38% NH$_4$NO$_3$
  - 18% (NH$_4$)$_2$SO$_4$
  - 42% Organic Compounds

  cf. Novakov and Penner, 1996

Ming and Russell, 2004
Less Hygroscopic Fog-CCN Number

- 122 total CCN
- 85% of CCN number are more-hygroscopic particles
- 15% of CCN number are less-hygroscopic particles
  - organic-dominated
  - with secondary nitrate

cf. Novakov and Penner, 1996
What is the “soluble” fraction?

<table>
<thead>
<tr>
<th>Water Soluble Organic Carbon Measurements</th>
<th>Equivalent Solubility g C/100g</th>
<th>Filter Loading µg C/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td>max</td>
</tr>
<tr>
<td>Mueller et al., 1982</td>
<td>7.0x10⁻⁴</td>
<td>1.1x10⁻¹</td>
</tr>
<tr>
<td>Kawamura and Ikushima, 1993</td>
<td>1.6x10⁻²</td>
<td>6.3x10⁻²</td>
</tr>
<tr>
<td>Kawamura et al., 1996</td>
<td>8.1x10⁻⁴</td>
<td>6.7x10⁻²</td>
</tr>
<tr>
<td>Facchini et al., 1999</td>
<td>8.2x10⁻⁴</td>
<td>1.8x10⁻²</td>
</tr>
<tr>
<td>Zappoli et al., 1999</td>
<td>1.8x10⁻³</td>
<td>6.7x10⁻³</td>
</tr>
<tr>
<td>Decesari et al., 2001</td>
<td>5.0x10⁻³</td>
<td>3.6x10⁻²</td>
</tr>
</tbody>
</table>

- Measured solubility uncertainty is a factor of 100+.
- Relevant solubility varies with RH and $S_c$. 

[Diagram showing Relative Humidity (RH) with Dissolution RH and Deliquescence RH regions]
FIGURE 11. FTIR-measured water-rinsed OM fraction immediately before, during, and immediately after rain events. A linear fit to the data ($y = 0.55 - 0.001t$) is shown as a dotted line.

Maria and Russell, unpublished
Precipitation Effects on Organic Aerosol

Total Aerosol

- aromatic
- alkane
- sulfate
- ammonium

Removed by Rain

Not Removed by Rain

Maria and Russell, unpublished
Hygroscopicity and Absorption

Randles, Russell, and Ramaswamy, submitted GRL
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Organic Carbon in Climate Models

Assumptions

Sensitivity Studies

Comparisons to Data

what we don’t know but we haven’t looked at

what we tested to see if it matters that we don’t know

how well it works despite what we don’t know
Organic Carbon in Climate Models

- Comparison to Data

Figure 11. Simulated OC concentrations versus observations for (a) IMPROVE sites, (b) rural sites, (c) remote sites, and (d) marine sites. The dashed lines indicate 10:1 and 1:10 ratios.

Chung and Seinfeld, 2002
ACE-Asia Comparison to Emissions Inventory

- Air mass group number
- 5-day modeled back trajectories
- 5-day weighted average from emissions inventory (Streets et al., 2003)
- Linear correlation to data
- Data
- Average 5-day back trajectory

Maria et al., 2003
CO/OC Characterization for ACE-Asia Backtrajectory Groups

Processed and Biomass  Mixed  Unprocessed and Automobiles

Maria et al., 2003
Processed Northwestern Asian Air Mass CO/OC

- Measured < Inventory
- Model or inventory limitations
- Secondary OC formation?
  - Organic functional groups indicate more oxidized groups

Maria et al., 2003
Organic Carbon Forcing

• Observations higher than simulations
  – Especially for remote/marine areas
  – May result from
    » Reaction/removal rates too fast?
    » Sources under-predicted?
    » Hygroscopic properties over/under-predicted?

• Implied OC contribution to forcing -0.2 W m²
  – With higher burden (Kanakidou et al., 2000) ~ -0.6 W m²
  – With lower rates (Maria et al., 2004) ~ -0.4 W m²
  – With absorption (Randles et al., 2004) > 0 W m²?