Atmos. Chem. Lecture 20, 11/25/13:
Aerosol chemistry (organic)

Jessica: Satellite measurements

Intro to organic aerosol
Partitioning, vapor pressures of organics
Modeling approaches for organic aerosol

Chemical composition of fine particulate matter

Zhang et al. 2007

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Climate-relevant properties of organics: Direct effect

Brown Carbon Spheres in East Asian Outflow and Their Optical Properties


See also Kirchstetter et al., JGR 109:D21208 (2004); Bond and Bergstrom, AS&T 40:27 (2006); Feng et al. ACP 13:8607 (2013)

Cappa et al.,
JGR 116:D15204 (2011)

Climate-relevant properties of organics: Indirect effect

Chang et al., Atm. Env. 41:8172 (2007)

Surface tension lowering:
Sareen et al., PRAS 110:2723 (2013)

Jimenez et al.,
Science 326:1525 (2009)

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Inorganic vs. organic aerosol

- **Inorganics**
  - Few components (SO$_2^-$, NO$_3^-$, NH$_4^+$...
  - Formed by well-established chemistry
  - Well-characterized properties
  - Relatively inert chemically
  - Generally well-represented in models

- **Organics**
  - 1,000's-10,000's of compounds (more?)
  - Formation chemistry uncertain
  - Properties highly variable
  - Reactive (oxidation reactions)
  - Very poorly described by models

- For more details, see Heald et al., GRL 32, L18809 (2005)
- Volkamer et al., GRL 33, L17811 (2006)

Chemical complexity of organics

See also
Example: diesel exhaust

→ 170 compounds measured, accounting for ~75% of mass
there are many more: "unresolved complex mixture"

→ diesel exhaust is a relatively simple system!

Sources of organic aerosol

Photochemical Oxidation → Secondary Organic Aerosol (SOA)

Primary Organic Aerosol (POA)

Gas-phase Emissions → Particulate Emissions

Terpenes → Aromatics

Biogenic Emissions → Anthropogenic Emissions

Biomass Burning

Depositional Sinks

Chemistry Transport

Dry Deposition

Vet Deposition

Image by MIT OpenCourseWare.

Hallquist et al., ACP 9:5155 (2009)
## Types of organic aerosol

<table>
<thead>
<tr>
<th>Primary vs. secondary OA</th>
<th>Anthropogenic vs. &quot;natural&quot; OA</th>
</tr>
</thead>
</table>
| Molecular markers: mostly POA  
  e.g. Cass et al.          | Consideration of VOC emissions: Biogenic  
  e.g., Goldstein and Galbally ES&T 41:1515 (2007) |
| OC/EC: high levels (~50%) in SOA  
  e.g., Lim and Turpin, ES&T 36:4489 (2002) | $^{13}$C ratios of OA: High modern fraction  
  e.g., Lemire et al., JGR 107:4613 (2002) |
| O/C ratios: mostly SOA, esp. rural areas  
  e.g., Zhang et al., GRL 34, L13801 (2007) | Correlation with tracers: Anthropogenic  
  e.g., De Gouw et al., 110:016305 (2005) |

### Blurring these distinctions

- see Carlton et al., ES&T 44:3376 (2010)

## Gas-particle partitioning of organics

$$X (g) \rightleftharpoons X (p)$$


[Note: Additional material is discussed here during lecture.]
Changes to saturation vapor pressure

1) oxidation reactions:

\[ \text{RCH}_3 \xrightarrow{\text{OH}} \text{RCH}_2 \xrightarrow{\text{O}_2} \text{RCH}_2\text{O}_2 \xrightarrow{\text{NO}} \text{RCH}_2\text{O} \xrightarrow{\text{O}_2} \text{RCHO} \]

- RCH$_3$: alkane
- RCH$_2$: alkyl radical
- RCH$_2$O$_2$: alkylperoxy radical
- RCH$_2$O: alkly radical
- RCHO: aldehyde

2) acid-base reactions
3) oligomerization/accretation reactions
4) temperature

Calculating saturation vapor pressures

Changes to vapor pressure of an organic compound upon addition of common functional groups, based upon group-contribution method predictions of Pankow and Asher (2007)

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Structure</th>
<th>Change in vapor pressure (298 K) $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ketone</td>
<td>$-\text{C(O)}-$</td>
<td>0.10</td>
</tr>
<tr>
<td>Aldehyde</td>
<td>$-\text{C(OH)}$</td>
<td>0.085</td>
</tr>
<tr>
<td>Hydroxyl</td>
<td>$-\text{OH}$</td>
<td>$5.7 \times 10^{-3}$</td>
</tr>
<tr>
<td>Hydroperoxyl</td>
<td>$-\text{OOH}$</td>
<td>$2.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>Nitrate</td>
<td>$-\text{ONO}_2$</td>
<td>$6.8 \times 10^{-3}$</td>
</tr>
<tr>
<td>Carboxylic acid</td>
<td>$-\text{C(OH)}$</td>
<td>$3.4 \times 10^{-4}$</td>
</tr>
<tr>
<td>Peroxyacid</td>
<td>$-\text{C(=O)OOH}$</td>
<td>$3.2 \times 10^{-3}$</td>
</tr>
<tr>
<td>Acyl peroxyxinate</td>
<td>$-\text{C(=O)OONO}_2$</td>
<td>$2.7 \times 10^{-3}$</td>
</tr>
<tr>
<td>Extra carbon$^b$</td>
<td>$-\text{CH}_2$- etc.</td>
<td>0.35$^b$</td>
</tr>
</tbody>
</table>

$^a$ Multiplicative factor.

SIMPOL: ACP 8:2773 (2008)


Many other structure-activity relationships as well e.g., EVAPORATION, Compernolle et al. ACP 11:9431 (2011)
Treating chemical complexity: Speciated approaches

(1) Explicit mechanisms
  e.g., Master Chemical Mechanism (MCM: mcm.leeds.ac.uk):
  near-explicit description of organic chemistry

(2) Self-generating schemes
  e.g., The Generator for Explicit Chemistry and Kinetics of Organics
  in the Atmosphere (GECKO-A)
  Aumont et al., ACP 5:2497 (2005)
  Camredon et al., ACP 7:5599 (2007)


Treating chemical complexity: Ensemble approach

“n-product model”
Odum et al., ES&T 30:2580 (1996)

\[ \text{HC} + \text{OH} \rightarrow \alpha_1 S_1 + \alpha_2 S_2 + \alpha_3 S_3 + \ldots \]

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Treating chemical complexity: Ensemble approach

“Volatility basis set”

\[ X_i (g) \rightleftharpoons X_i (p) \]

\[ F_p = K_p M_o / (1 + K_p M_o) \]

**terminology:**
- \( c^* = 1/K_p \)
- \( c_{OA} = M_o \)

see also Robinson et al., *Science* 315:1259 (2007)
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Gas-particle equilibrium?

**An amorphous solid state of biogenic secondary organic aerosol particles**


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