Organic Aerosols in the Gulf of Maine: Perspective from the 2002 New England Air Quality Study

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1. Quantitative separation of different POM sources primary and secondary, anthropogenic and biogenic

2. Organic carbon as a function of photochemical age gas and particle phase
New England Air Quality Study (NEAQS) in 2002

Ship-based measurements off the U.S. East coast during July-August 2002

NOAA Ronald H. Brown

New York City
Boston
Charleston
Measurements of Organic Carbon during NEAQS

Particle phase:
Sub-μm organic matter (POM)
Sub- and super-μm organic carbon (POC)

AMS Middlebrook
Impactors Bates

- POM and POC correlated: \( r = 0.93 \)
- POM/POC = \( 1.78 \pm 0.13 \)
- Super-μm < 20% of sub-μm POC
**Gas phase**:

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Instrument</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOCs</td>
<td>PTR-MS</td>
<td>de Gouw</td>
</tr>
<tr>
<td>VOCs, alkyl nitrates</td>
<td>GC-MS</td>
<td>Goldan</td>
</tr>
<tr>
<td>PANs</td>
<td>GC-ECD</td>
<td>Roberts</td>
</tr>
<tr>
<td>Organic acids</td>
<td>MC-IC</td>
<td>Keene, Pszenny</td>
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</tbody>
</table>

Gas-phase measurements inter-compared [de Gouw et al., JGR 2003]

<table>
<thead>
<tr>
<th>Date</th>
<th>Toluene (ppbv)</th>
<th>Isoprene (ppbv)</th>
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<tbody>
<tr>
<td>7/13/02</td>
<td>1.2</td>
<td>0.8</td>
</tr>
<tr>
<td>7/17/02</td>
<td>0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>7/21/02</td>
<td>0.4</td>
<td>0.0</td>
</tr>
<tr>
<td>7/25/02</td>
<td>0.0</td>
<td>0.0</td>
</tr>
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</table>
Particulate organic matter (POM) was the dominant sub-\(\mu\)m species.

also observed by Quinn and Bates [GRL 2003]

What are the sources of POM in New England?
Suggests most of the POM was secondary from anthropogenic precursors

- What about primary emissions of POM?
- What about biogenic precursors of POM?
Primary Sources of POM

POM shows minor enhancements close to urban sources.
Biogenic Sources of POM

Minor POM enhancements downwind of large biogenic sources
Biogenic Sources of POM

Minor POM enhancements downwind of large biogenic sources
Benzene and toluene are emitted from vehicles at a constant ratio
Toluene is 4.8× faster removed than benzene
Primary Anthropogenic VOCs versus Photochemical Age

Ethyl benzene is more reactive than acetylene ⇒ ratio decreases with age
Comparison of Emission Ratios

At zero age: VOC composition equals that of average U.S. city
Iso-Propyl Nitrate versus Photochemical Age

Fit: Propane assumed to be precursor
Yield (only free parameter) 3.7%
Literature value 2.9%
Enhancement of POM versus acetylene increases as the air mass is processed.

Importance of secondary POM formation.
Quantitative Separation of VOC and POM Sources

Basic assumptions:

1. Primary anthropogenic emissions of VOCs and POM are proportional to those of acetylene

2. Removal of primary anthropogenic VOCs and POM, and formation of secondary anthropogenic species is governed (i) by the photochemical age and, as much as possible, (ii) by the reaction kinetics

3. Primary and secondary biogenic contributions of VOCs and POM are proportional to the emissions of isoprene
Separation of the POM Sources

Primary anthropogenic: 6%
Secondary anthropogenic: 66%
Biogenic: 6%
Background: 22%

Tracers used in the fit:
- Acetylene
- Isoprene

Fit results:
- Photochemical age
- Isoprene emitted (ppbv)
- Sub-μm POM (μg m⁻³)

Calculation (ppbv): 16
Measurement (μg m⁻³): 12

r=0.76
The higher the secondary fraction of the POM, the more processed the particles were according to the AMS.
POM, OVOCs and PANs increase with age; the rest decreases.
Total organic carbon approximately conserved.
Decrease of ~40% due to deposition?
Secondary POC yield = \[\sum_{i=1}^{32} [\text{alkanes}]_i Y_i + \sum_{j=1}^{13} [\text{aromatics}]_j Y_j + \sum_{k=1}^{10} [\text{alkenes}]_k Y_k\]

where \(Y_i\) is the potential yield for species \(i\) [Seinfeld and Pandis].

- alkanes \(0.09\)
- aromatics \(0.34\)
- alkenes \(0.00\)
- total \(0.43 \, \mu g \, C \, m^{-3} \, (ppbv \, C_2H_2)^{-1}\)

Less than 10% of secondary formation of POC can be attributed to known precursors!
What does it mean?

1. Are other precursors more important?
   - 80% of species in vehicle exhaust was measured
   - Paulson et al.: 85% of TOC can be identified by GC

2. Formation of secondary POM continues longer than accounted for by smog-chamber experiments?

3. Is the biogenic contribution properly accounted for?
   - Radiocarbon dating of POM typically gives higher modern fraction
   - POM formation from biogenic precursors may be more efficient in polluted conditions
Conclusions

- POM in New England region was mostly attributed to secondary anthropogenic sources
- The primary and biogenic fractions of POM were surprisingly small
- The total mass of organic carbon decreased by ~40% in the first 2 days after emission
- The increase in POC could not be explained by the decrease in known precursors
## Acknowledgements

### Measurements
- **AMS**: Ann Middlebrook, Doug Worsnop, Manjula Canagaratna
- **EC/OC**: Tim Bates
- **PTR-MS**: Carsten Warneke
- **GC-MS**: Paul Goldan, Bill Kuster
- **PANs**: Jim Roberts, Matt Marchewka, Steve Bertman
- **MC-IC**: Bill Keene, Alex Pszenny

### Project management
- Tim Bates, Fred Fehsenfeld, Jim Meagher, Eric Williams

### Crew of the NOAA *Ronald H. Brown*
Can we separate Secondary Anthropogenic and Secondary Biogenic Sources?

Perform same analysis for PANs:

Williams et al. 1998:
PPN: secondary anthropogenic
MPAN: secondary biogenic
PAN: both

This analysis:

<table>
<thead>
<tr>
<th></th>
<th>Primary Anthropogenic</th>
<th>Secondary Anthropogenic</th>
<th>Biogenic</th>
</tr>
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<tbody>
<tr>
<td>PPN</td>
<td>0%</td>
<td>97%</td>
<td>3%</td>
</tr>
<tr>
<td>MPAN</td>
<td>0%</td>
<td>14%</td>
<td>86%</td>
</tr>
<tr>
<td>PAN</td>
<td>0%</td>
<td>75%</td>
<td>25%</td>
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Analysis of PANs confirms that secondary anthropogenic and secondary biogenic sources are mostly separated by the method.