Atmospheric Aerosols from Biogenic Hydrocarbon Oxidation

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Jana Milford

Department of Mechanical Engineering
University of Colorado, Boulder
Acknowledgments

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* Coauthor
Outline

- Background
  - Biogenic hydrocarbon emissions and secondary organic aerosol (SOA) formation
  - Sesquiterpenes (SQTs) and monoterpenes (MTs)
- Project objectives
- Methods
  - Chemical transport modeling
  - Measurements
  - Emissions modeling
- Results
  - Emissions comparisons
- Conclusions
Sesquiterpene (SQT) and Monoterpene (MT) Emissions from Vegetation

Monoterpenes $\text{C}_{10}\text{H}_{16}$
Sesquiterpenes $\text{C}_{15}\text{H}_{24}$

- Significant emissions
  - North America total Monoterpene emissions 17.9 Tg C yr$^{-1}$
    (Guenther et al., 2000)
  - Sesquiterpene emissions?
- Highly reactive
- Oxidation products can partition to the aerosol phase
<table>
<thead>
<tr>
<th>Parent terpenoid</th>
<th>Aerosol Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta^3$-Carene</td>
<td>2.3 – 10.9</td>
</tr>
<tr>
<td>$\beta$-Caryophyllene</td>
<td>17.2 – 62.5</td>
</tr>
<tr>
<td>$\alpha$-Humulene</td>
<td>20.0 – 66.7</td>
</tr>
<tr>
<td>Limonene</td>
<td>6.1 – 22.8</td>
</tr>
<tr>
<td>Myrcene</td>
<td>7.6 – 12.7</td>
</tr>
<tr>
<td>$\alpha$-Pinene</td>
<td>2.4 – 7.8</td>
</tr>
<tr>
<td>$\beta$-Pinene</td>
<td>4.2 – 13.0</td>
</tr>
<tr>
<td>Sabinene</td>
<td>4.7 – 10.6</td>
</tr>
</tbody>
</table>

Griffin et al., 1999
Key Questions

- What are the regional landscape fluxes of MTs and SQTs?
  - Environmental controls
  - Spatial and temporal variations

- What is the contribution of BVOC oxidation to SOA formation in the eastern U.S.?
  - Diurnal and seasonal trends
  - Differences in the contributions from MTs and SQTs

- How sensitive is secondary aerosol formation from BVOC to anticipated changes in:
  - Process model assumptions?
  - Emissions of nitrogen oxides?
  - Land cover?
Regional Chemical Transport Modeling

- **MM5/CMAQ**
- **Domain Resolution**
  - Horizontal: 36 km x 36 km
  - Vertical layers: 9
- **Chemical Mechanism**
  - SAPRC99 with 3rd generation aerosol model and aqueous chemistry
- **Episodes**
  - July 2001
  - January 2002
CMAQ Modifications

- SAPRC99 mechanism with aqueous chemistry and aerosol module
- BCARL, AHUMUL, SQST with $O_3$, $NO_3$, and OH

- Aerosol Yields
- Partitioning Parameters
- Aerosol Properties
- BCARL, AHUMUL, and SQST

- Photooxidation
- Chemical Reactions
- Advection
- Dry Deposition
- Wet Deposition

- Incorporate SQTs into other processes
- New SQT emissions
- MEGAN model
CMAQ Inputs

**Initial Conditions**
- Last hour output

**Meteorological Data – MM5**
- July 2001
- January 2002

**Boundary Conditions**
- MOZART2.2 output
  - Louisa Emmons

**Anthropogenic Emissions Data**

**SMOKE 2.0 (U.S.) - NEI 1999**
- Area, Point, Mobile, Nonroad, and Point sources
  - July 2001
  - January 2002

**SMOKE 2.1 - Mexico (1999), Canada (1996)**
- Area, Point, Mobile, Nonroad, and Point sources
  - July 2001
  - January 2002

T. Russell and Sun-Kyoung Park (GA. Tech)
Model Evaluation: Focus on Eastern U.S.

- **Supersites**
  - Atlanta, Baltimore, NY, Pittsburgh, St. Louis
  - intensive periods
    - July 2001, January 2002

- **IMPROVE**
  - 24 h avg PM2.5, SO$_4^{2-}$, NO$_3^-$, OC, EC

- **SEARCH**
  - urban/rural pairs in AL, FL, GA, MI
  - C-14 data at three sites

- TVA C-14 data (Look Rock, TN)
Biogenic Emissions Inventory Development

MEGAN
Emission Model

Guenther, A.

Land Use & Cover

MM5
Meteorological Data

Emission Data

Helmig et al., and Harley, P.
Measurement of SQT and MT emissions

- Bag and cuvette enclosure systems
- Calibration system
  - Helmig et al., 2003
- Cartridge and on-line sampling
- GC-MS, GC-PTRMS, GC-FID
- Laboratory and field measurements
Branch enclosure measurements at Duke Forest (summer – fall 2004)

- Loblolly pine
- Four FEB Teflon film branch enclosure systems operated simultaneously
  - Two tower
  - Two ground-level
- Double ozone scrubbing in all experiments
- Aromatic doping used to test recoveries
- Possible 5-10% wall loss for SQT
Chromatogram (plotted as the flame ionization detector (FID) response) from a ponderosa pine emission sample. Monoterpene retention times 7.2–14.7 min; sesquiterpene retention times 18.9-22.5 min. Shaded peaks are the aromatic compounds from the reference standard.

Helmig et al., ES&T, 41:1545, 2007
Prominent Sesquiterpenes in Recent Measurements

1. β-Caryophyllene

2. α/β- Bergamotene

3. β-Farnesene

4. α-Farnesene

5. α-Humulene

6. α-Muurolene

7. Germacrene D

8. Δ-Cadinene

9. β-Selinene

10. γ-Cadinene

Helmig et al., in progress

Atkinson and Arey, 2003, Griffin et al., 1999
Sesquiterpene (SQT) emission rate (ER) data from an enclosure experiment on a loblolly pine tree at Duke Forest showing total SQT emission rates plotted against the mean needle temperature inside the enclosure. Helmig et al., ES&T, 41:1545, 2007
BVOC Emissions Modeling: MEGAN

- Model of Emissions of Gases and Aerosols from Nature: MEGAN
  - 1 km resolution
  - Improved evaluation of LAI and Land Cover inputs
  - Available through the NCAR Community Data Portal

\[
EM = \varepsilon \cdot \gamma_{CE} \cdot \gamma_{age} \cdot \gamma_{SM} \cdot \rho
\]

\[
\gamma_{CE} = \gamma_{LAI} \cdot \gamma_{P} \cdot \gamma_{T}
\]

- \( EM \): Emission (\( \mu g \, m^{-2} \, hr^{-1} \))
- \( \varepsilon \): Emission Factor (\( \mu g \, m^{-2} \, hr^{-1} \))
- \( \rho \): Loss and Production within plant canopy
- \( \gamma_{CE} \): Canopy Factor
- \( \gamma_{age} \): Leaf Age Factor
- \( \gamma_{SM} \): Soil Moisture Factor
- \( \gamma_{LAI} \): Leaf Area Index Factor
- \( \gamma_{P} \): PPFD Emission Activity Factor (light-dependence)
- \( \gamma_{T} \): Temperature Response Factor

Guenther, 2006
MEGAN v2.0

Meteorological Data
- Temperature
- Solar Radiation

Grid Information
X
Y

Land Cover Data
4 PFT categories
- Needle leaf
- Broad leaf
- Shrub-Bush
- Grass-Herb
Fractions of plants in grid cells

Emission Factors
\( \gamma_{CE} \), \( \gamma_{age} \), \( \gamma_{SM} \), \( \gamma_{LAI} \), \( \gamma_{P} \), \( \gamma_{T} \)

Speciation & Mechanism Conversion
1) CBMZ
2) SAPRC99
3) RACM
4) RADM2

Emissions Data

I/O API - NETCDF
- Linux REDHAT WS
- FORTAN PGF90
- IOAPI 3.0
- NETCDF 3.5.1

ASCII format

I/O API - NETCDF
MEGAN v. BEIS3

- Additional emission activity algorithms
  - Sensible heat flux, leaf age, long term effects of temperature and PAR
- Simplified canopy model to account for leaf temperature and canopy light extinction
- Updated emissions factors
  - Includes speciated SQT and MT emissions from measurements
  - EF for individual chemical species vary spatially
- Multiple options for landcover inputs including high resolution satellite data (MODIS, SPOT)
Basal SQT and MT Emissions Rates for Needle Leaf Trees

Helmig et al., 2007, Matsunaka, Potosnak et al.
Creekside Nursery
June – Aug. 2006

NCAR Greenhouse
Aug. 2006

Helmig and Daly, 2007
### NCAR SQT Measurement Comparison, April 30 - May 4, 2007

<table>
<thead>
<tr>
<th>Participants</th>
<th>Affiliation</th>
<th>Sample Collection</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detlev Helmig</td>
<td>CU/INSTAAR</td>
<td>On-line On-line Tenax adsorbent</td>
<td>GC-MS GC-FID GC-FID</td>
</tr>
<tr>
<td>Peter Harley</td>
<td>NCAR</td>
<td>Tenax adsorbent</td>
<td>GC-FID</td>
</tr>
<tr>
<td>Alex Guenther</td>
<td>NCAR</td>
<td>On-line</td>
<td>GC-MS</td>
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<tr>
<td>Thomas Karl</td>
<td>NCAR</td>
<td>On-line</td>
<td>PTR-MS</td>
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<tr>
<td>Jim Greenberg</td>
<td>NCAR</td>
<td>On-line</td>
<td>O3 Reactivity</td>
</tr>
<tr>
<td>Sou Matsunaga</td>
<td>NCAR</td>
<td>Super Q</td>
<td>GC-FID</td>
</tr>
<tr>
<td>Tiffany Duhl</td>
<td>NCAR</td>
<td>Super Q</td>
<td>GC-FID</td>
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<tr>
<td>Monica Madronich</td>
<td>NCAR</td>
<td>Super Q</td>
<td>GC-FID</td>
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<tr>
<td>Nicole Bouvier-Brown</td>
<td>UC Berkeley</td>
<td>SPME Fibers</td>
<td>GC-MS</td>
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<tr>
<td>Rei Rasmussen</td>
<td>Oregon Health &amp; Science Univ.</td>
<td>Tenax adsorbent Canisters</td>
<td>GC-MS GC-MS; GC-FID</td>
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<tr>
<td>Chris Geron Bob Arnts</td>
<td>USEPA</td>
<td>Tenax adsorbent</td>
<td>GC-MS</td>
</tr>
<tr>
<td>Hannele Hakola</td>
<td>Finnish Meteor. Institute</td>
<td>Tenax adsorbent</td>
<td>GC-FID</td>
</tr>
</tbody>
</table>

Courtesy of P. Harley
Comparison of SQT Emission Factors from Recent Measurements v. Prior Literature

Recent data

MEGAN2.0-06b SQT

MEGAN2.0-L SQT

Literature through 2004

Emission Factors for 4 PFTs

- Broadleaf
- Needle Leaf
- Shrub-Bush
- Grass-Crop

ug/m²-hr
SQT and MT Emission Factors by Plant Functional Type

- **MEGAN2.0-06b SQT**
  - Recent data

- **MEGAN2.0-L SQT**
  - Literature through 2004

- **MEGAN2.0 MTP**
  - Recent data
Emissions Modeling Results -- January

**BEIS 3.0**

**Layer 1, SQT**
BEIS3.0 (0.2 TRP1 mass + 0.15 OBJVOC mass) January Monthly Average

**Layer 1, MTP**
BEIS3.0 (0.8 TRP1 mass) January Monthly Average

**MEGAN2.0-06b**

**Layer 1, SQT**
MEGAN2.0-06b (BCAL+AHUMUL+SSQT) January Monthly Average

**Layer 1, MTP**
MEGAN2.0-06b (TRP1) January Monthly Average

**MEGAN2.0-L**

**Layer 1, SQT**
MEGAN2.0-L (BCAL+AHUMUL+SSQT) January Monthly Average

**Layer 1, MTP**
MEGAN2.0-06b (TRP1) January Monthly Average

Max 465.8 g/km²-hr Max 154.4 g/km²-hr Max 154.4 g/km²-hr
Emissions Modeling Results – July

BEIS 3.0

Layer 1, SQT
BEIS3.0 (TRP1 and OBVOC) 0.2 TRP1 mass + 0.15 OBVOC in July Monthly Average

MEGAN2.0-06b

Layer 1, SQT
MEGAN2.0-06b (BCARL+AHUMUL+SSQT) July Monthly Average

MEGAN2.0-L

Layer 1, SQT
MEGAN2.0-L (BCARL+AHUMUL+SSQT) July Monthly Average

Layer 1, MTP
BEIS3.0 (TRP1) 0.8 TRP1 mass July Monthly Average

Layer 1, MTP
MEGAN2.0-06b (TRP1) July Monthly Average
Emissions Modeling Results

SOA Precursor Speciation for SAPRC99-S, July Average Emissions - CMAQ Domain

BEIS3.0, MEGAN2.0-06b, MEGAN2.0-L

TRP1, SSQT, AHUM UL, BCARL, CRES, ARO2, ARO1, OLE2, OLE2, ALK5
Conclusions

- SQT emissions are highly variable
  - Emissions likely dependent on leaf age and other environmental variables
  - Seasonal dependence is uncertain but maybe important
- Measured SQTs appear to have stronger temperature dependency than MT emissions
- Light-dependency observed in some MTs and SQTs
- Some crops appear to be strong SQT emitters – need more measurements
- MEGAN provides an easily adaptable framework for BVOC emissions estimation
- Speciation schemes available for most popular chemical mechanisms
- SQT estimated to contribute 7 – 16% of SOA precursor emissions (anthropogenic and biogenic, excluding isoprene) for continental U.S. in July
- SQT estimated to contribute 1 – 2% of SOA precursor emissions in January
- SOA contributions to be determined!
Disclaimer

Although the research described in this presentation has been funded in part by the United States Environmental Protection Agency, it has not been subjected to the Agency’s required peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.