Atmospheric Aerosols from Biogenic Hydrocarbon Oxidation

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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 $C_{10}H_{16}$
Sesquiterpenes $C_{15}H_{24}$

- 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

\[\text{β-Caryophyllene}\]

\[\text{α-pinene}\]
Aerosol yields for biogenic MTs and SQTs

<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
- Incorporate SQTs into other processes
- Aerosol Yields
- Partitioning Parameters
- Aerosol Properties
- BCARL, AHUMUL and SQST
- Chemical Reactions
- Advection
- Dry Deposition
- Wet Deposition
- Deposition
- Emissions
- Photooxidation
- New SQT emissions
- MEGAN model
CMAQ Inputs

Initial Conditions
- Last hour output

Meteorological Data – MM5
- July 2001
- January 2002

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

Boundary Conditions
- MOZART2.2 output
- Louisa Emmons

- T. Russell and Sun-Kyoung Park (GA. Tech)

- 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

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

Emission Factors
- LAI

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
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.
SQT and MT Emissions Rates Summer 2006

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</td>
<td>GC-MS, GC-FID</td>
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<tr>
<td></td>
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<td>On-line Tenax adsorbent</td>
<td>GC-FID</td>
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<tr>
<td>Peter Harley</td>
<td>NCAR</td>
<td>Tenax adsorbent</td>
<td>GC-FID</td>
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<tr>
<td>Alex Guenther</td>
<td>NCAR</td>
<td>On-line</td>
<td>GC-MS</td>
</tr>
<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>
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<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-FID</td>
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<td>Chris Geron Bob Arnts</td>
<td>USEPA</td>
<td>Tenax adsorbent</td>
<td>GC-MS</td>
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<tr>
<td>Hannele Hakola</td>
<td>Finnish Meteor. Institute</td>
<td>Tenax adsorbent</td>
<td>GC-FID</td>
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</tbody>
</table>

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

Emission Factors for 4 PFTs

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

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

<table>
<thead>
<tr>
<th>Emission Factors</th>
<th>ug/m²-hr</th>
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<tr>
<td>Broadleaf</td>
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<tr>
<td>Needle Leaf</td>
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<tr>
<td>Shrub-Bush</td>
<td></td>
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<tr>
<td>Grass-Crop</td>
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**PFTs:***
- Broadleaf
- Needle Leaf
- Shrub-Bush
- Grass-Crop
SQT and MT Emission Factors by Plant Functional Type

Emission Factors for 4 PFTs

ug/m²-hr

MEGAN2.0-06b SQT
MEGAN2.0-L SQT
MEGAN2.0 MTP

Recent data
Literature through 2004
Recent data

Broadleaf
Needle Leaf
Shrub-Bush
Grass-Crop

Recent data Literature through 2004 Recent data
Emissions Modeling Results -- January

BEIS 3.0

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

Layer 1, SQT
MEGAN2.0-06b (BCAR1+AHUMUL+SSQT)
January Monthly Average

Layer 1, SQT
MEGAN2.0-L (BCAR1+AHUMUL+SSQT)
January Monthly Average

Layer 1, MTP
BEIS3.0 (0.8 TRP1 mass)
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  MEGAN2.0-06b  MEGAN2.0-L

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

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

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

Layer 1, MTP
MEGAN2.0-L (TRP1) July Monthly Average
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.