# Atmospheric Aerosols from Biogenic Hydrocarbon Oxidation

**Atmospheric Science Progress Review Meeting**

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# Outline

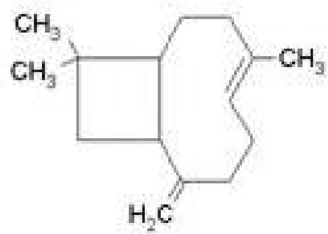
- Background
  - Biogenic hydrocarbon emissions and secondary organic aerosol (SOA) formation
  - Sesquiterpenes (SQTs) and monoterpenes (MTs)
- Project objectives
- Methods
  - Chemical transport modeling
  - Measurements
  - Emissions modeling
- Results
  - Emissions comparisons
- Conclusions

# Sesquiterpene (SQT) and Monoterpene (MT) Emissions from Vegetation

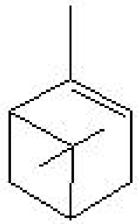
Monoterpenes $C_{10}H_{16}$
Sesquiterpenes $C_{15}H_{24}$

- 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




β-Caryophyllene



α-pinene

# Aerosol yields for biogenic MTs and SQTs

| Parent terpenoid | Aerosol Yield (%) |
|---|---|
| $\Delta^3$-Carene | 2.3 – 10.9 |
| β-Caryophyllene | 17.2 – 62.5 |
| α-Humulene | 20.0 – 66.7 |
| Limonene | 6.1 – 22.8 |
| Myrcene | 7.6 – 12.7 |
| α-Pinene | 2.4 – 7.8 |
| β-Pinene | 4.2 – 13.0 |
| Sabinene | 4.7 – 10.6 |

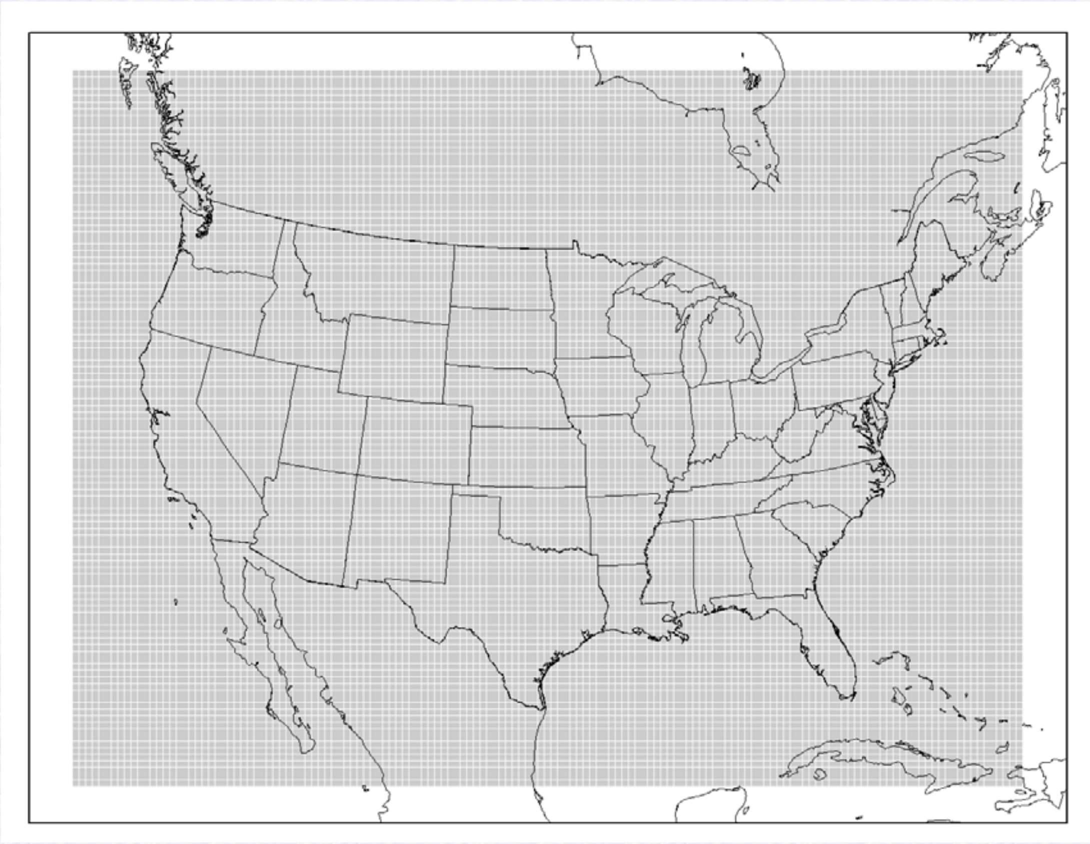
Griffin et al., 1999

# Key Questions

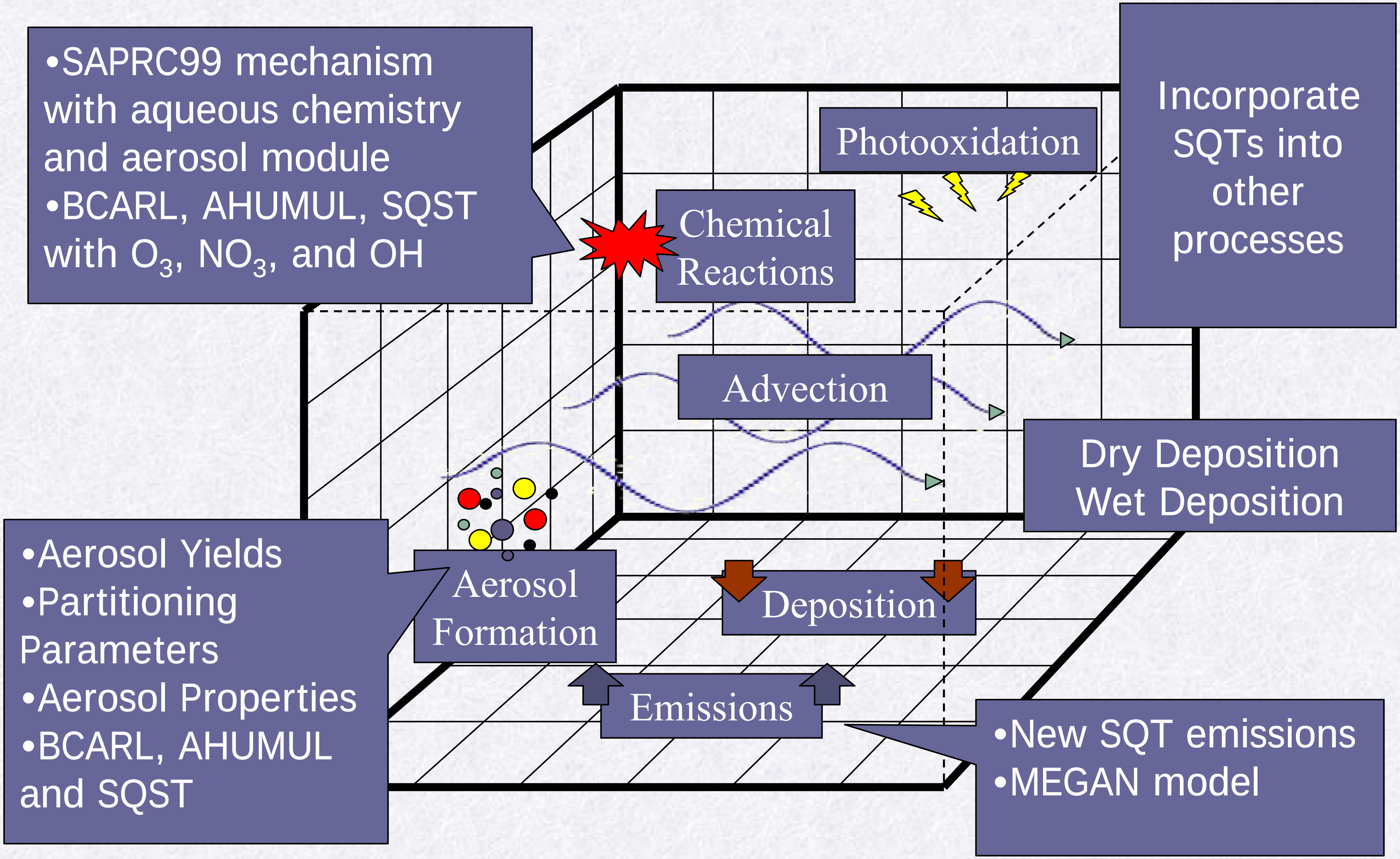
- What are the regional landscape fluxes of MTs and SQTs?
  - Environmental controls
  - Spatial and temporal variations
- What is the contribution of BVOC oxidation to SOA formation in the eastern U.S.?
  - Diurnal and seasonal trends
  - Differences in the contributions from MTs and SQTs
- How sensitive 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



# CMAQ Inputs

## Initial Conditions

- Last hour output

## Boundary Conditions

- MOZART2.2 output

Louisa Emmons

## Meteorological Data – MM5

- July 2001
- January 2002

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

## Anthropogenic Emissions Data

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

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

# 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, $SO_4^{=}$, $NO_3^{-}$, 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

Helmig et al., and Harley, P.

Land Use

& Cover

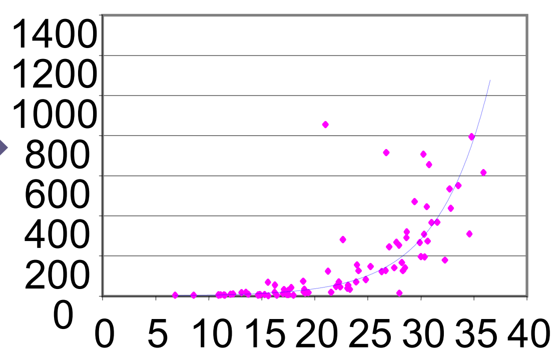
Guenther, A.

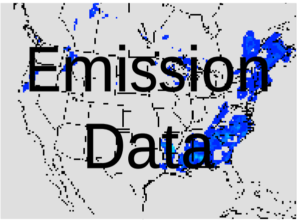
MEGAN

Emission Model

MM5

Meteorological Data



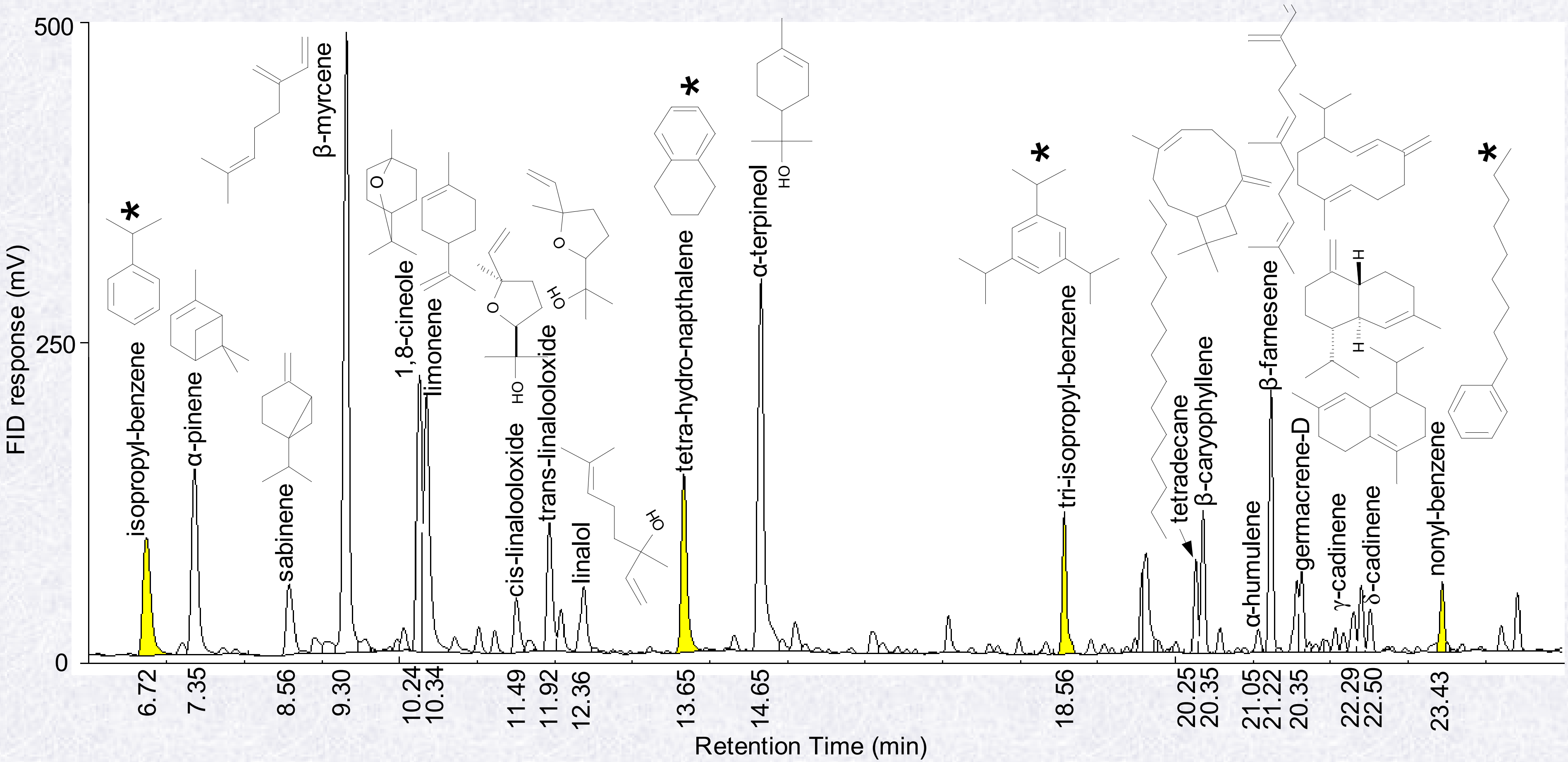



# Measurement of SQT and MT emissions

- 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

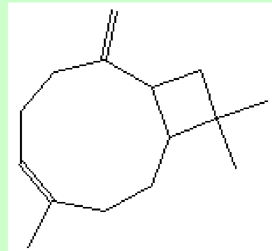



Chromatogram (plotted as the flame ionization detector (FID) response) from a ponderosa pine emission sample. Monoterpene retention times 7.2–14.7 min; sesquiterpene retention times 18.9-22.5 min. Shaded peaks are the aromatic compounds from the reference standard.

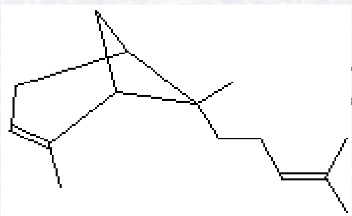
Helmig et al., ES&T, 41:1545, 2007

# Prominent Sesquiterpenes in Recent Measurements

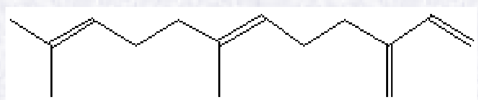
1. β-Caryophyllene



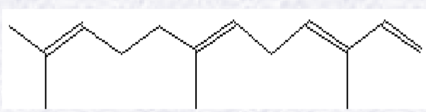
2. α/β- Bergamotene



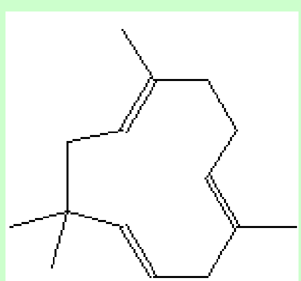
3. β-Farnescene



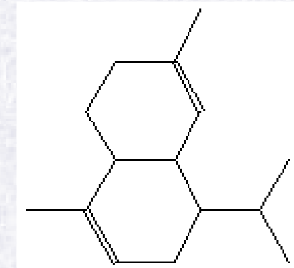
4. α-Farnescene



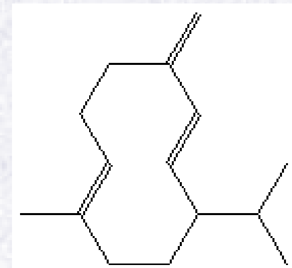
5. α-Humulene



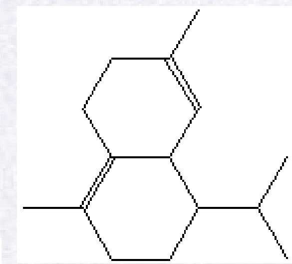
6. α-Muurolene



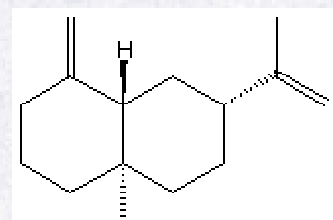
7. Germacrene D



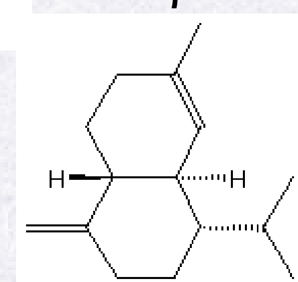
8. Δ-Cadinene



9. β-Selinene

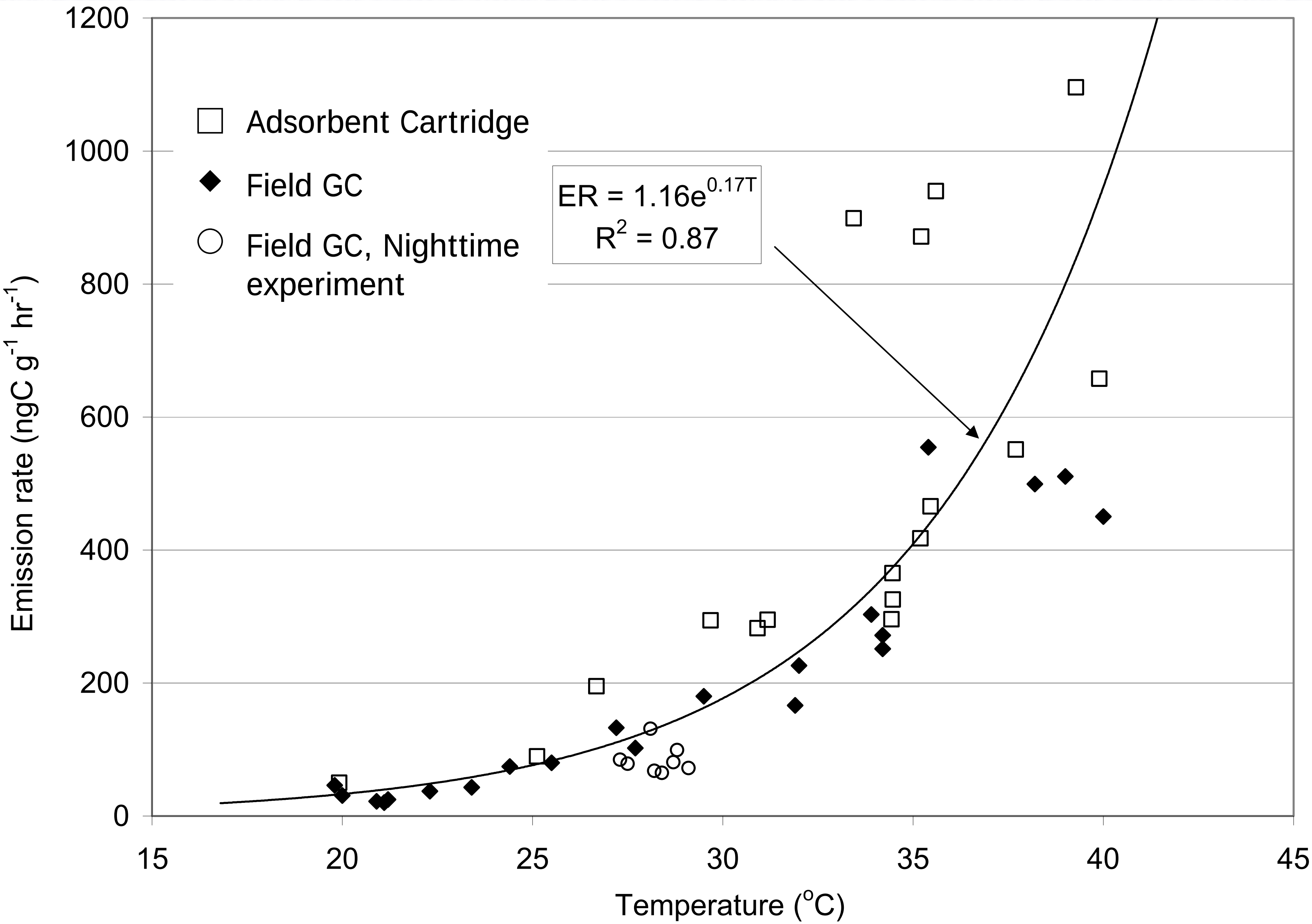



10. γ-Cadinene




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

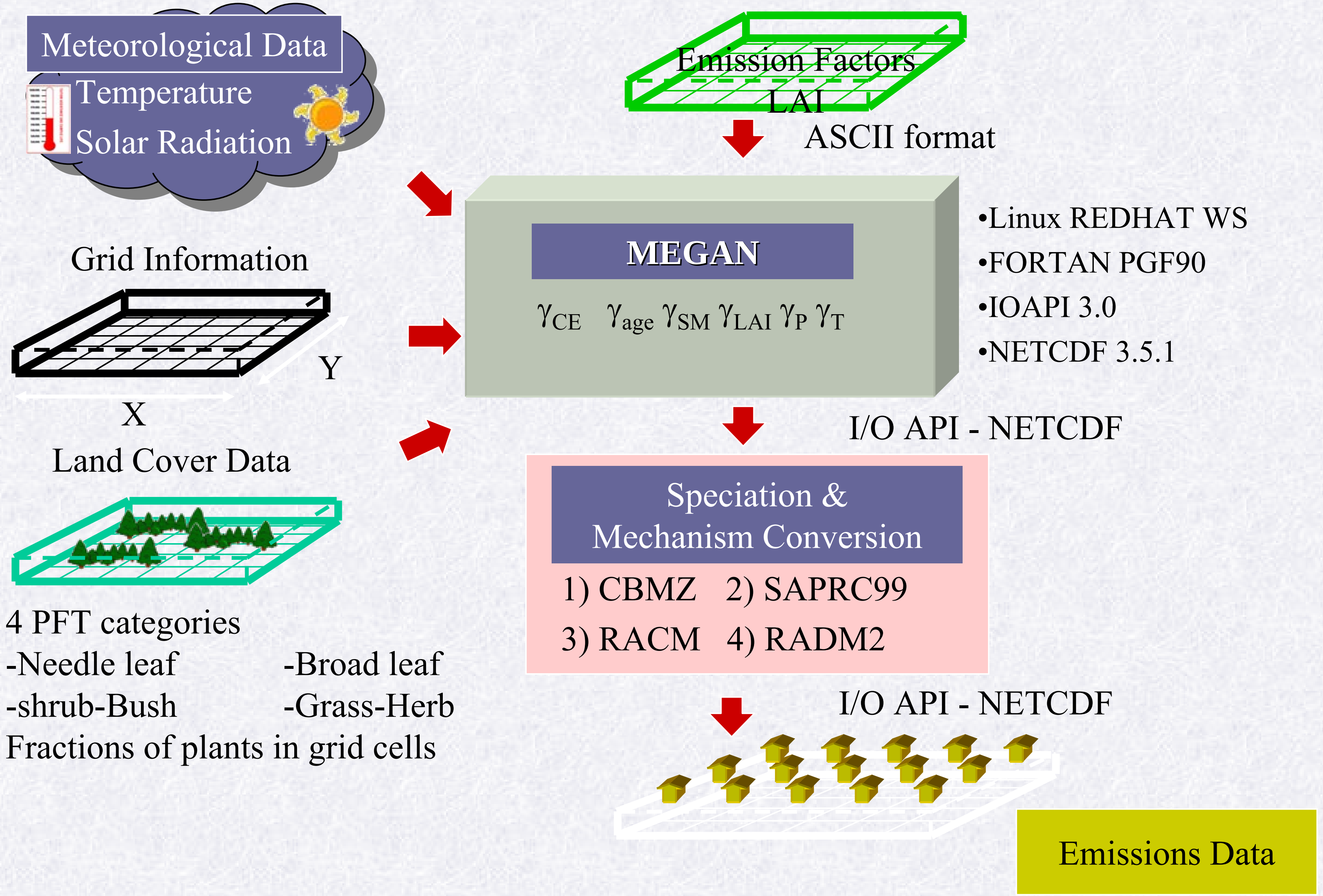
$$EM = \varepsilon \bullet \gamma_{CE} \bullet \gamma_{age} \bullet \gamma_{SM} \bullet \rho$$

$$\gamma_{CE} = \gamma_{LAI} \bullet \gamma_{P} \bullet \gamma_{T}$$

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

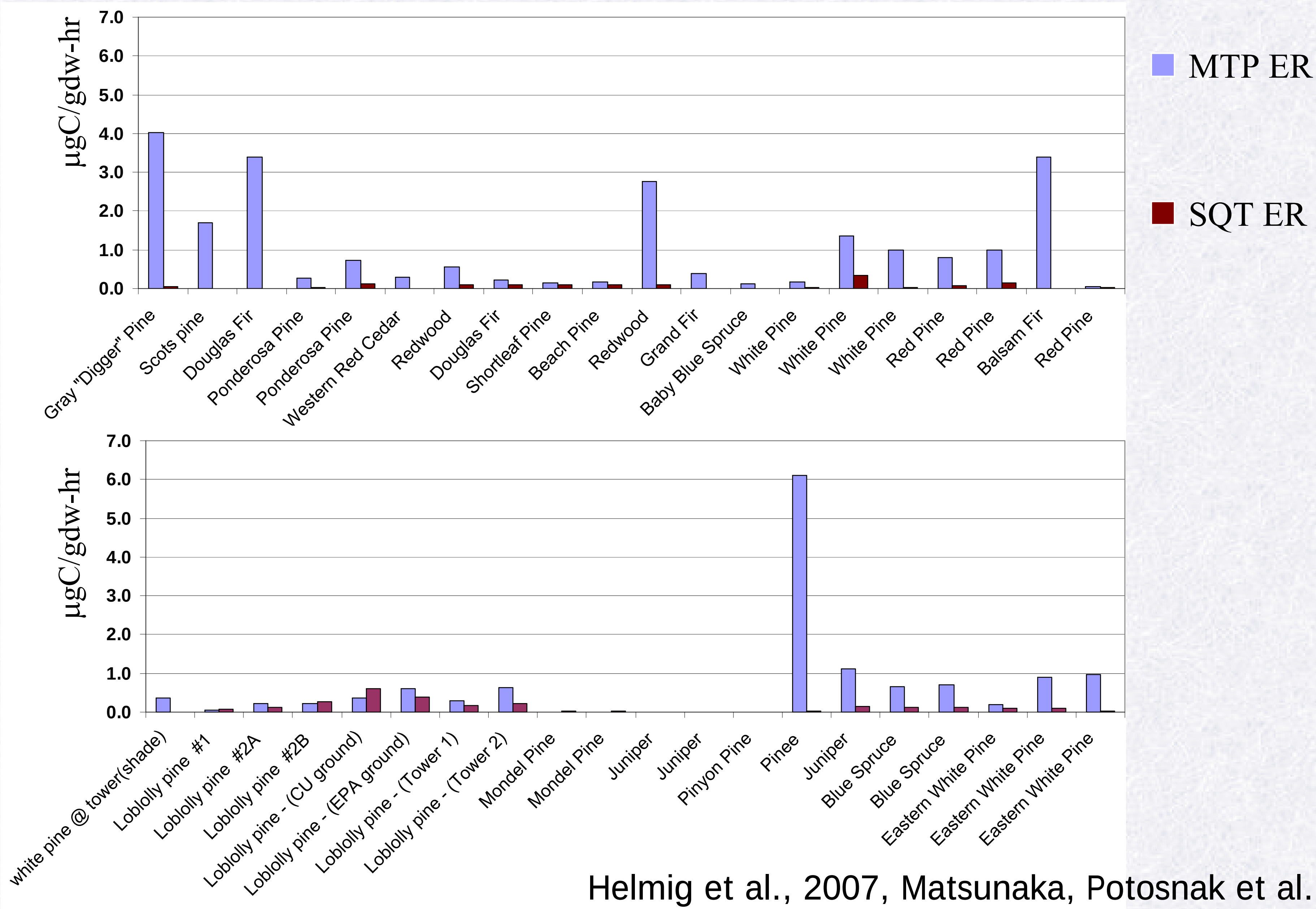


Meteorological Data
Temperature
Solar Radiation
Emission Factors
LAI
ASCII format
Grid Information
Y
X
MEGAN
$\gamma_{CE}$ $\gamma_{age}$ $\gamma_{SM}$ $\gamma_{LAI}$ $\gamma_{P}$ $\gamma_{T}$
•Linux REDHAT WS
•FORTAN PGF90
•IOAPI 3.0
•NETCDF 3.5.1
I/O API - NETCDF
Land Cover Data
Speciation & Mechanism Conversion
1) CBMZ 2) SAPRC99
3) RACM 4) RADM2
4 PFT categories
-Needle leaf -Broad leaf
-shrub-Bush -Grass-Herb
Fractions of plants in grid cells
I/O API - NETCDF
Emissions Data

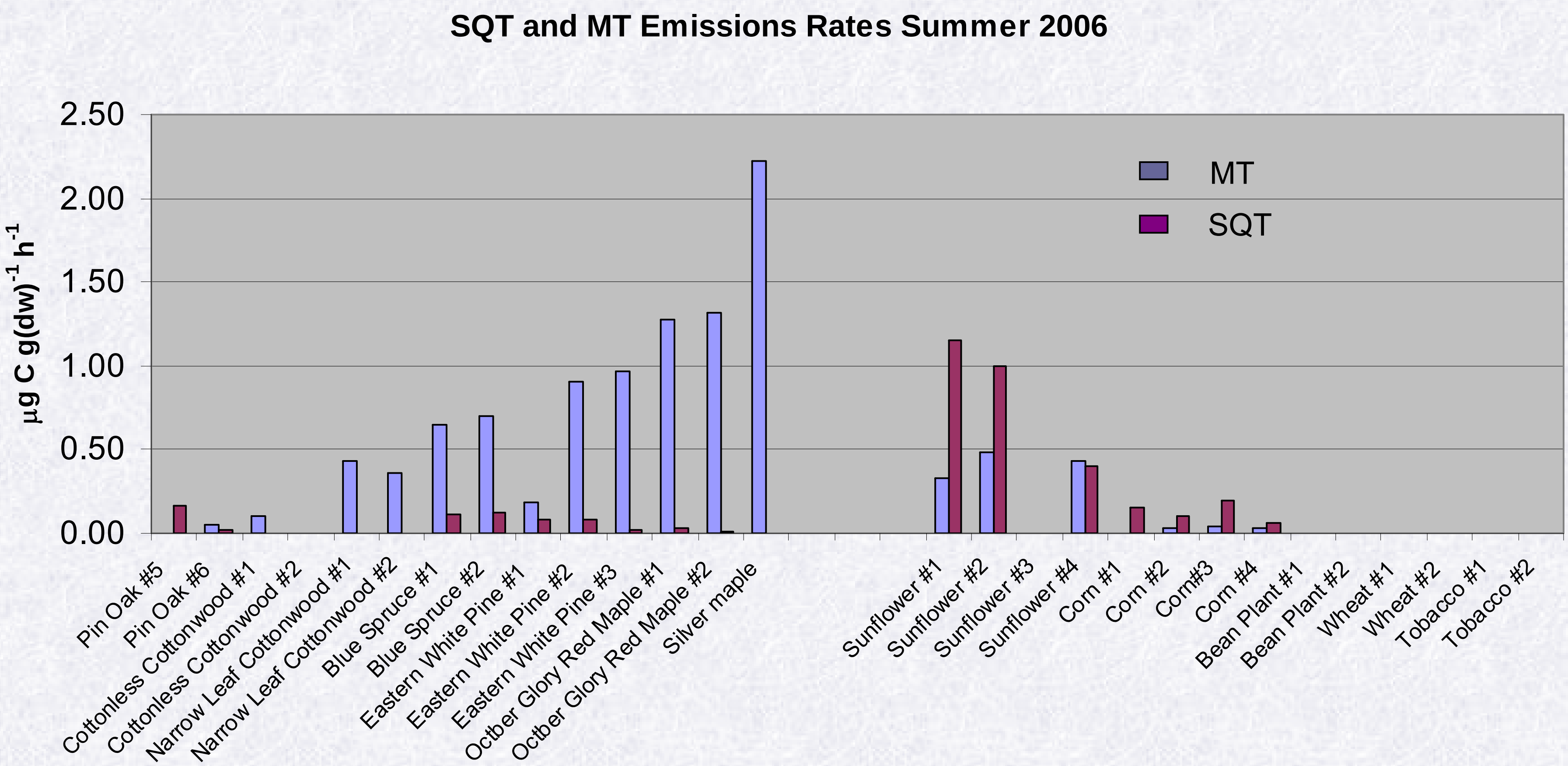
# MEGAN v. BEIS3

- 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

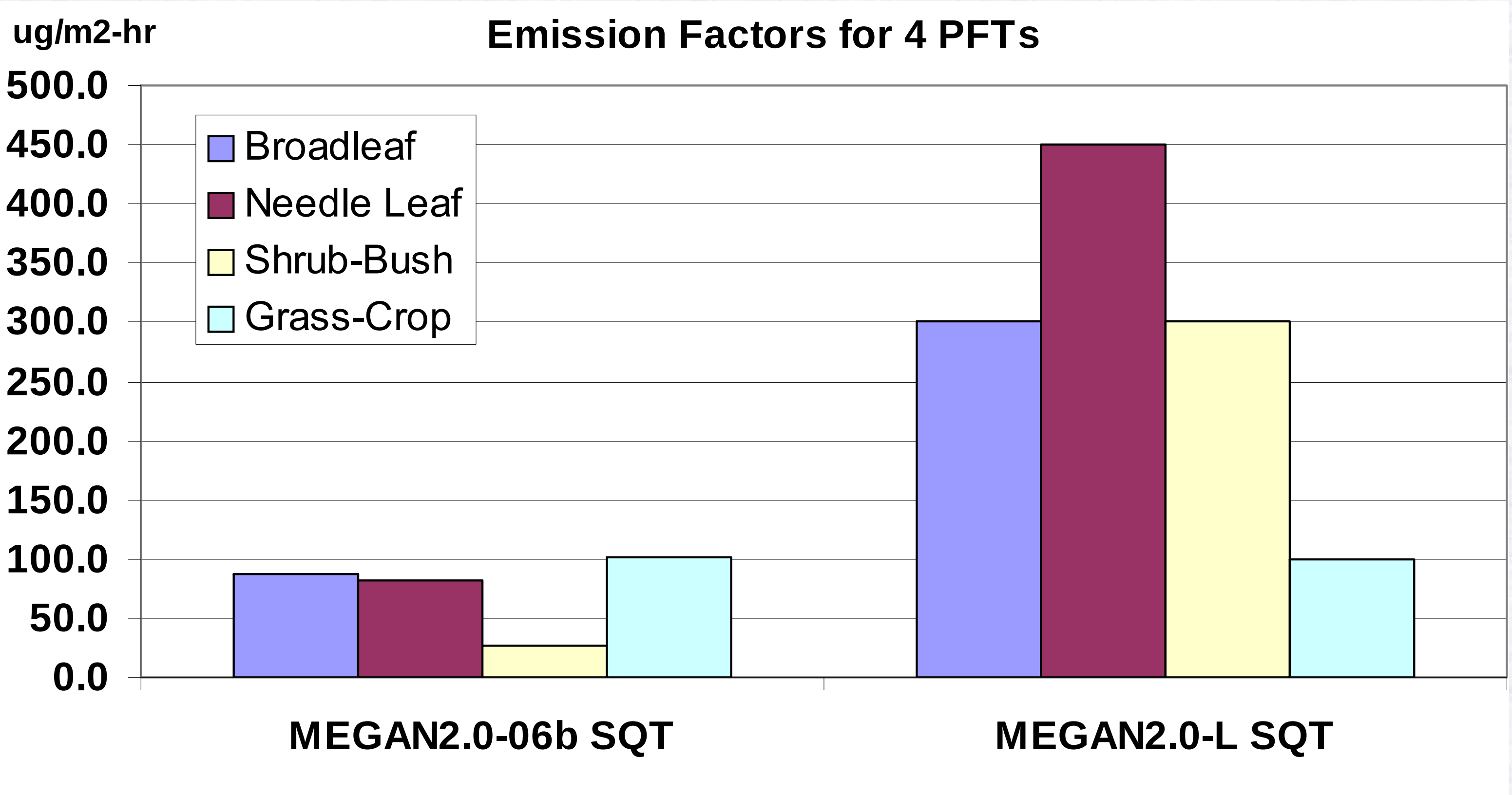
Helmig and Daly, 2007

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

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

Courtesy of P. Harley

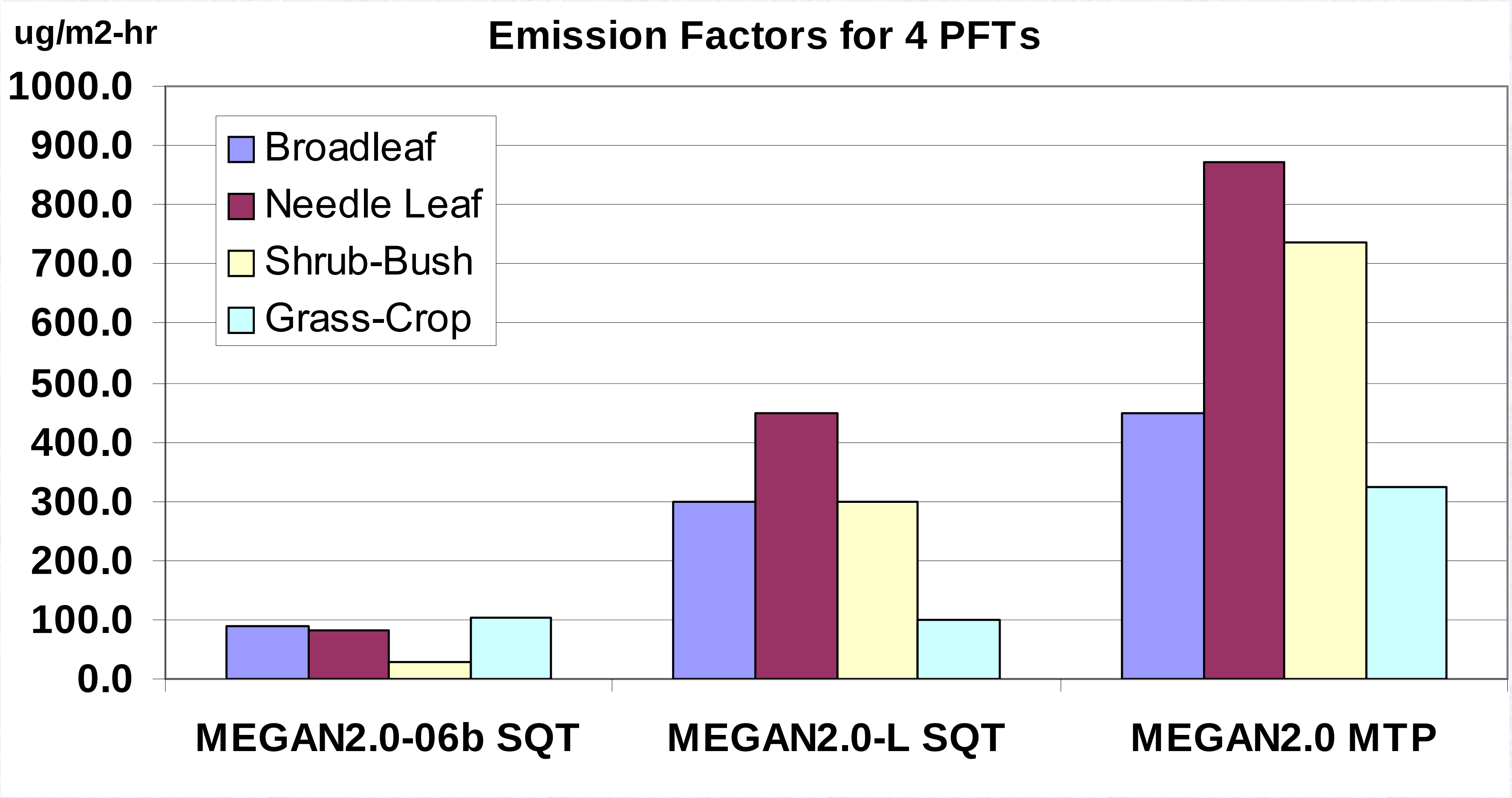
# Comparison of SQT Emission Factors from Recent Measurements v. Prior Literature




Recent data

Literature through 2004

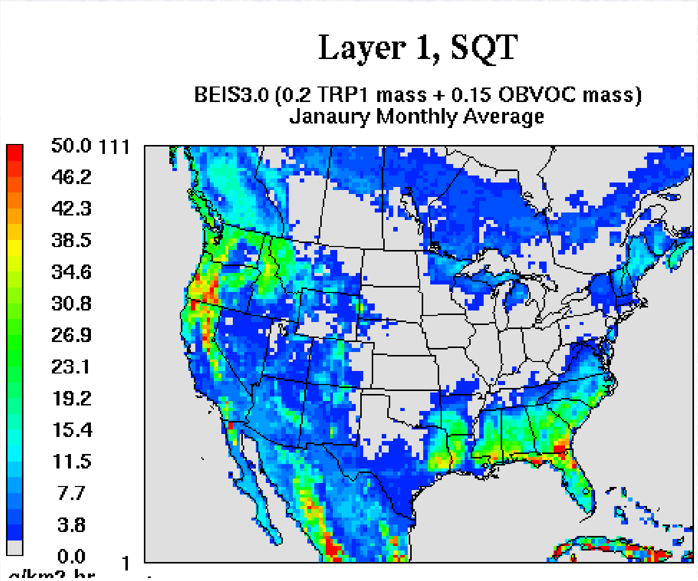
# SQT and MT Emission Factors by Plant Functional Type

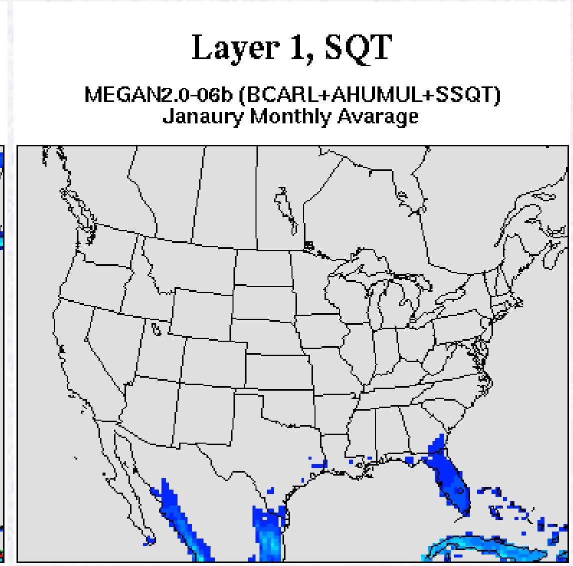


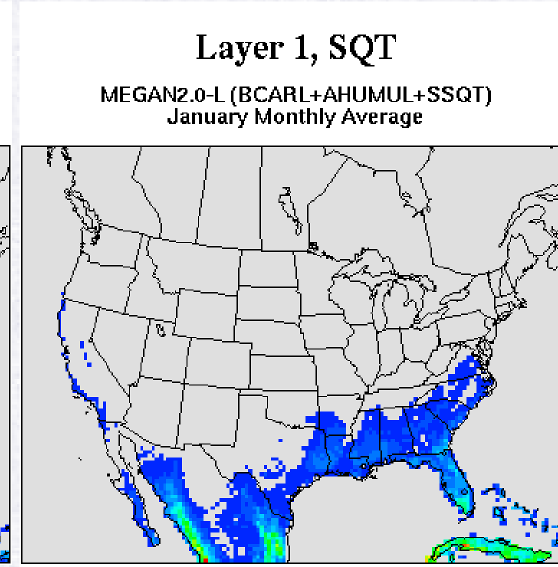

Recent data | Literature through 2004 | Recent data

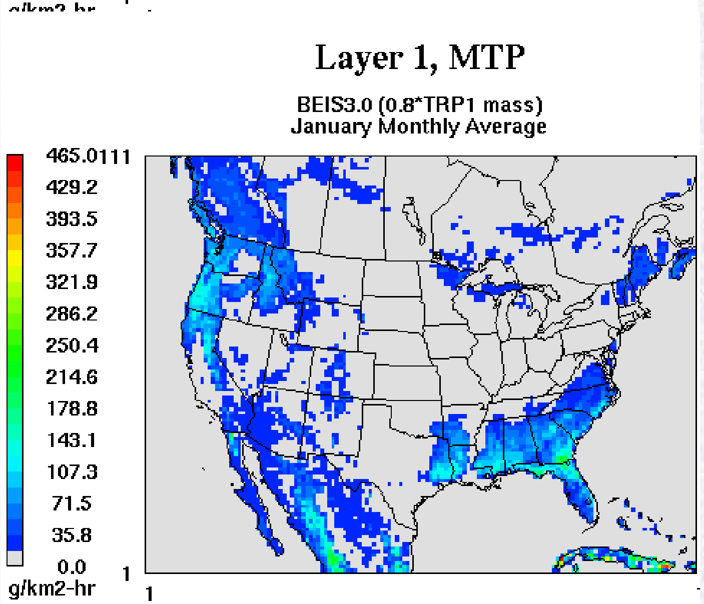
# Emissions Modeling Results -- January

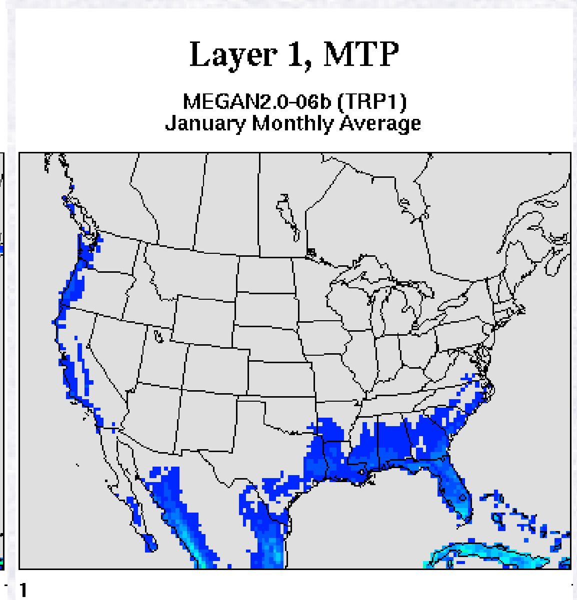
BEIS 3.0 | MEGAN2.0-06b | MEGAN2.0-L



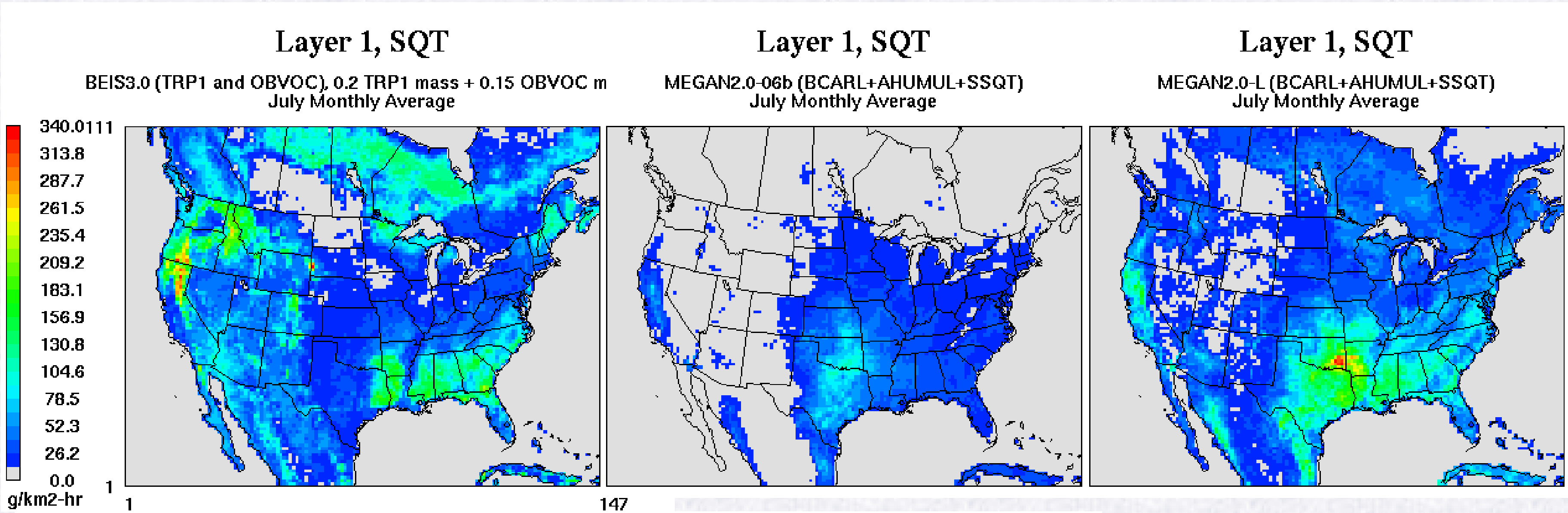



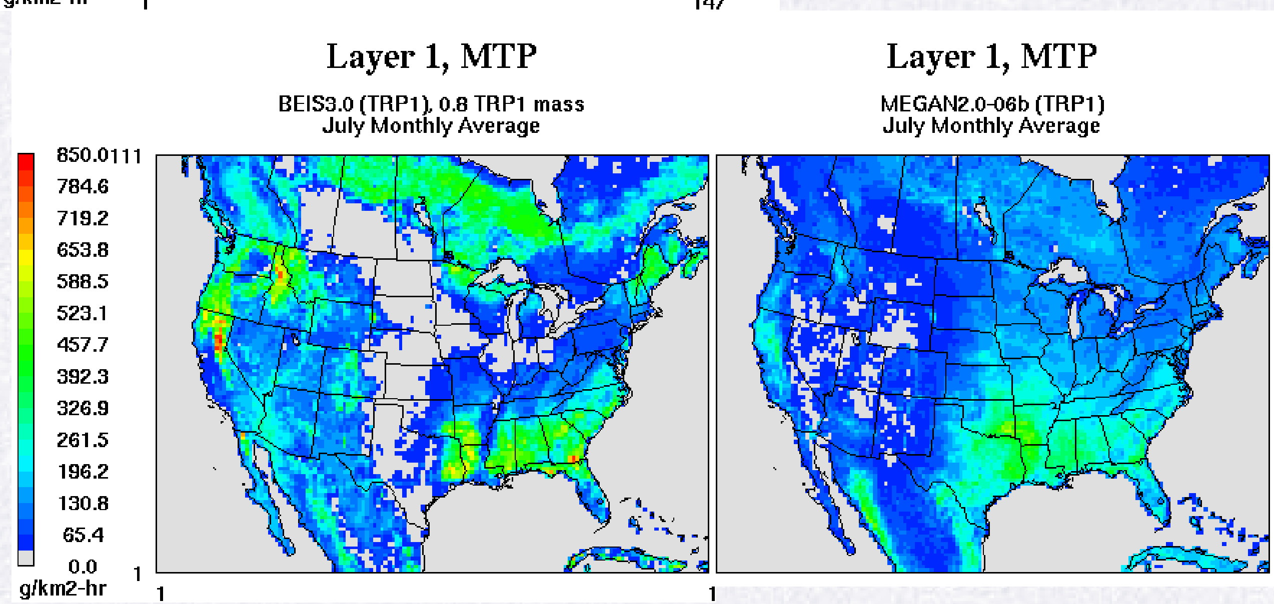




Max 465.8 g/km2-hr | Max 154.4 g/km2-hr | Max 154.4 g/km2-hr

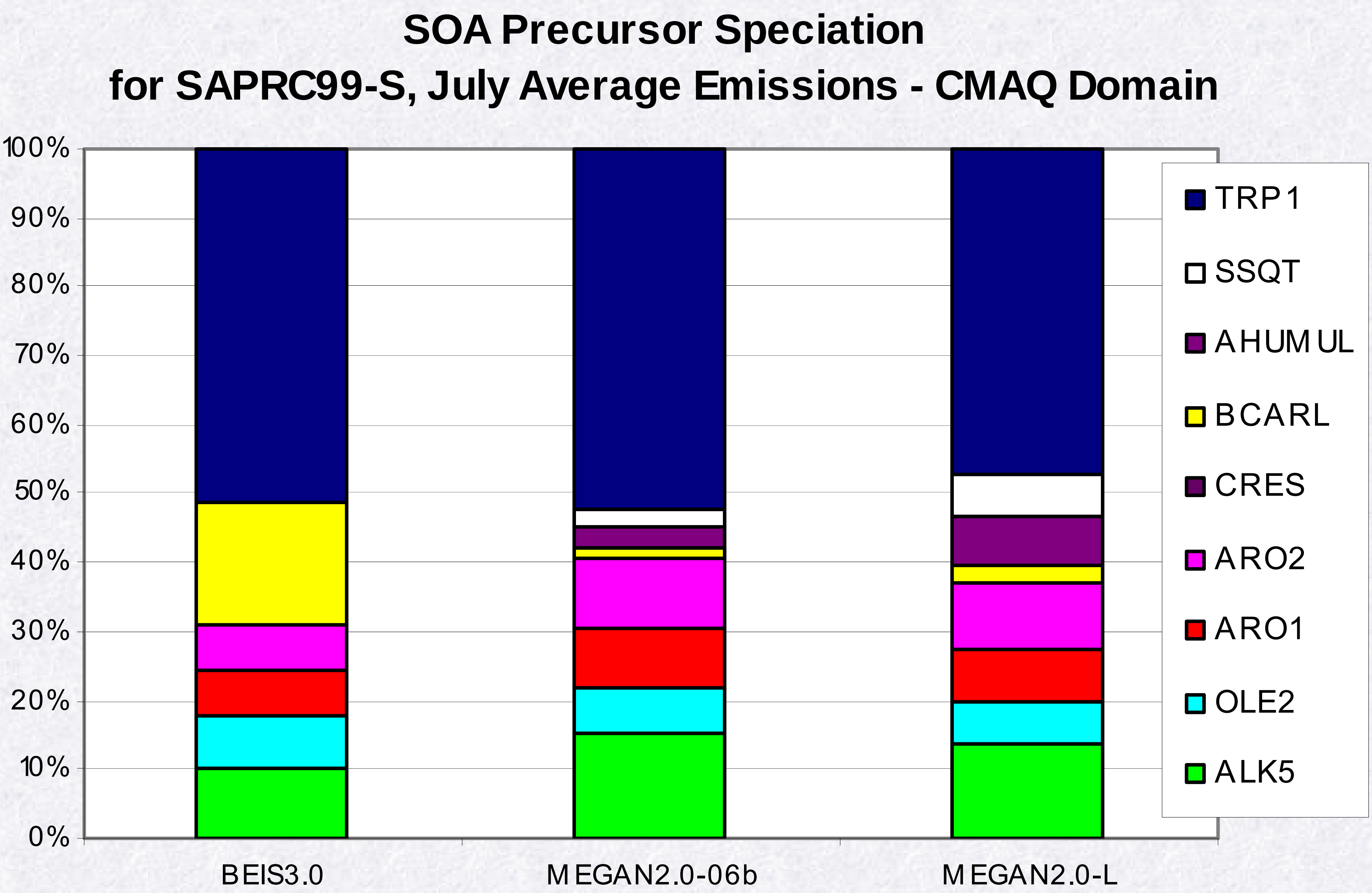
# Emissions Modeling Results – July

BEIS 3.0 MEGAN2.0-06b MEGAN2.0-L



# Emissions Modeling Results



# 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.