Atmospheric Aerosols from Biogenic Hydrocarbon Oxidation

Atmospheric Science Progress Review Meeting

June 21-22, 2007

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Acknowledgments

- Tanarit Sakulyanontvittaya,* CU-Boulder, Mechanical Engineering
- Detlev Helmig,* Tiffany Duhl, Ryan Daly, John Ortega, David Tanner, CU-Boulder, Institute for Arctic and Alpine Research
- Christine Wiedinmyer,* Alex Guenther,* Peter Harley,* John Orlando, Louisa Emmons, Sou Matsunaka, National Center for Atmospheric Research
- Bob Arnts, Chris Geron, Jeff Herrick, J. Harvey, U.S. Environmental Protection Agency
- Mark Potosnak, Desert Research Institute
- Bill Stockwell, Howard University
- Greg Yarwood, Environ
- Raoul Zavari, Pacific Northwest National Laboratory
- Ted Russell, Helena Park, Georgia Tech
- Gail Tonneson, University of California at Riverside
- NSF, Atmospheric Chemistry Program (ATM #0304704) and the U.S. EPA (#RD-83107901-0).

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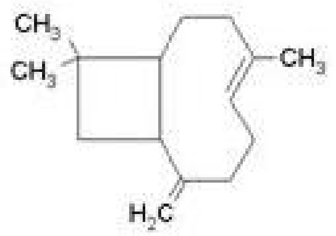
Outline

- 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

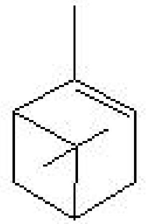
Monoterpenes $C_{10}H_{16}$
Sesquiterpenes $C_{15}H_{24}$



β-Caryophyllene

- 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



α-pinene

Aerosol yields for biogenic MTs and SQTs

Parent terpenoid	Aerosol Yield (%)
Δ^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

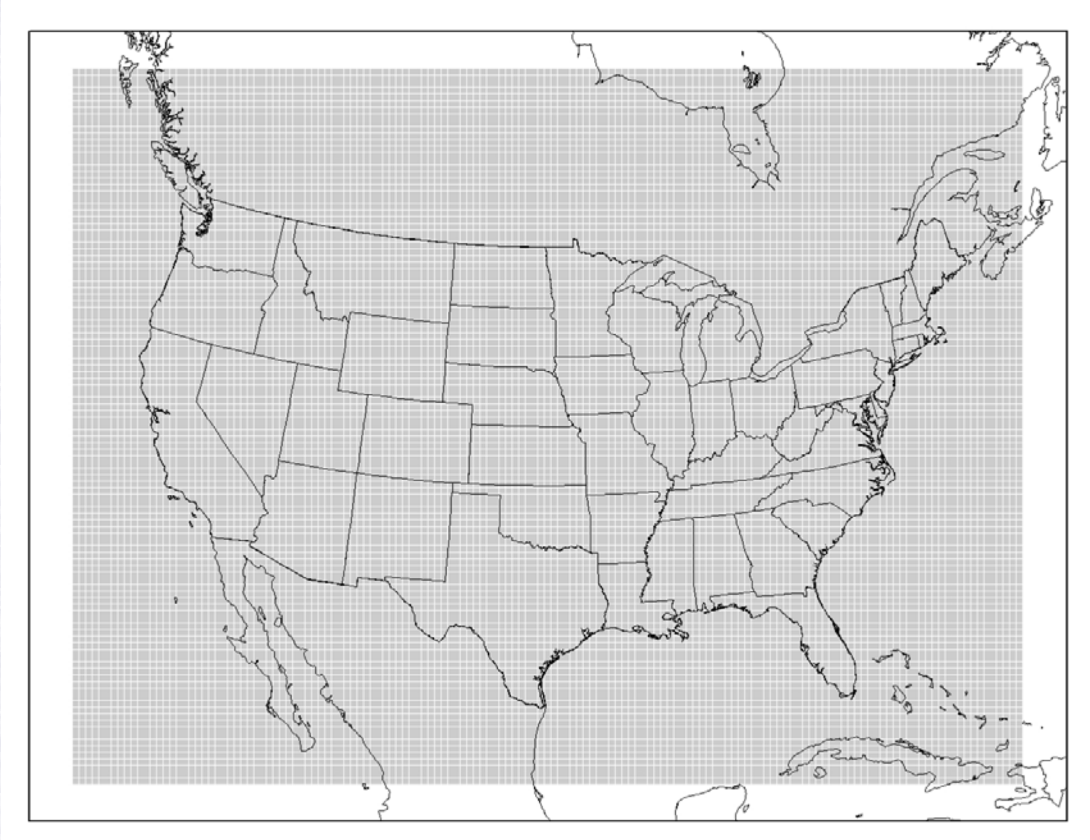
Griffin et al., 1999

Key Questions

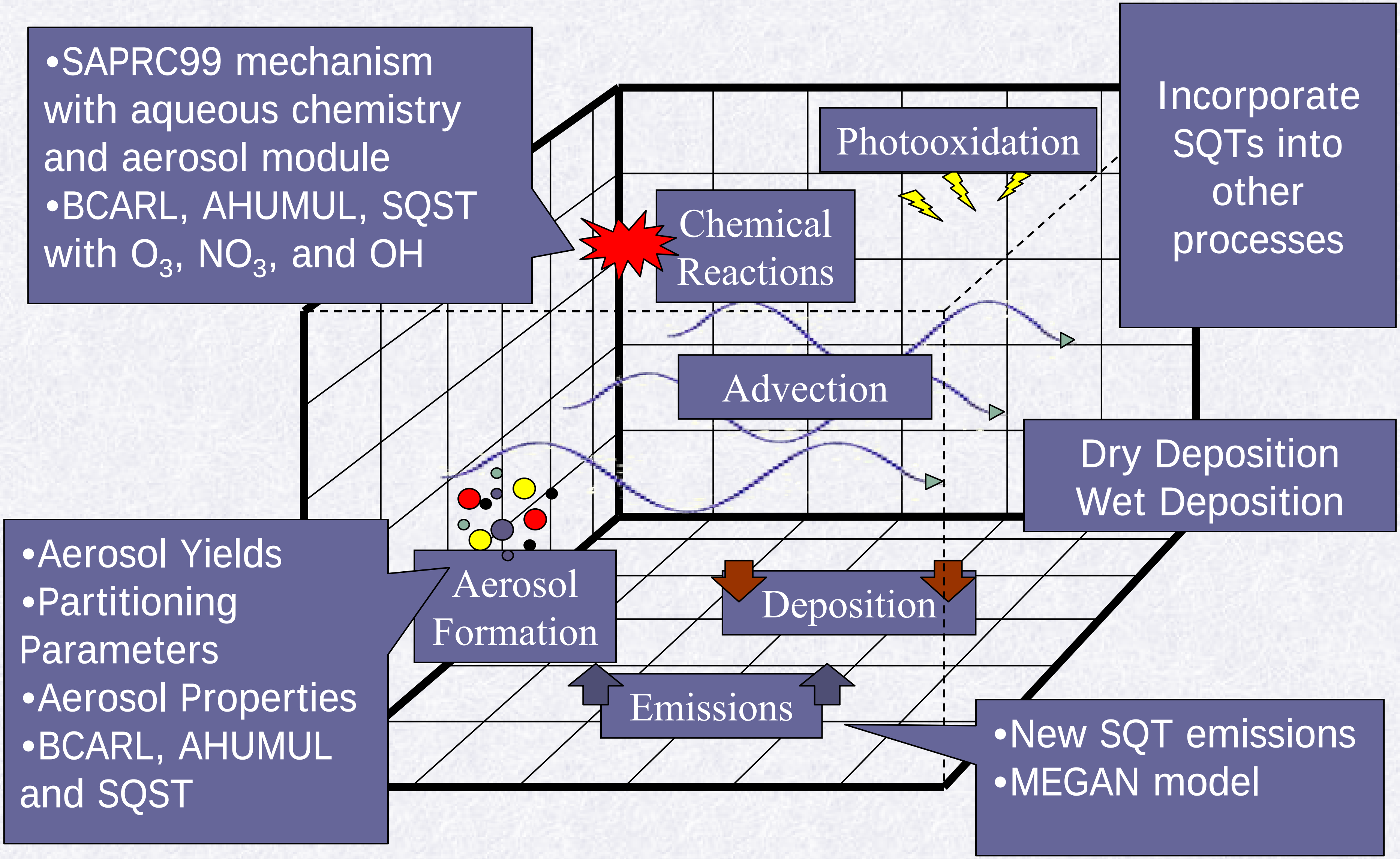
- What are the regional landscape fluxes of MTs and SQTs?
  - Environmental controls
  - Spatial and temporal variations
- What is the contribution of BVOC oxidation to SOA formation in the eastern U.S.?
  - Diurnal and seasonal trends
  - Differences in the contributions from MTs and SQTs
- How sensitive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

Guenther, A.

MEGAN

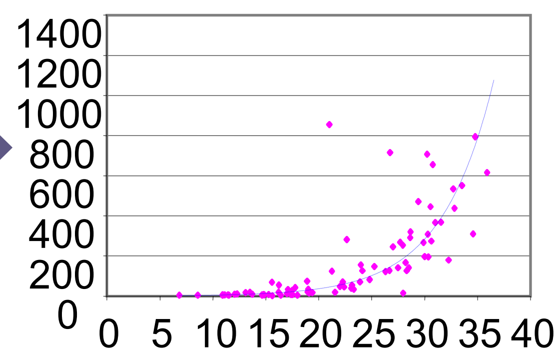
Emission Model

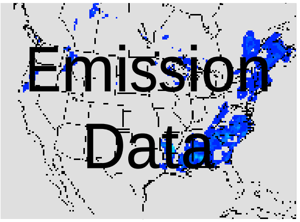
Land Use

& Cover

MM5

Meteorological Data



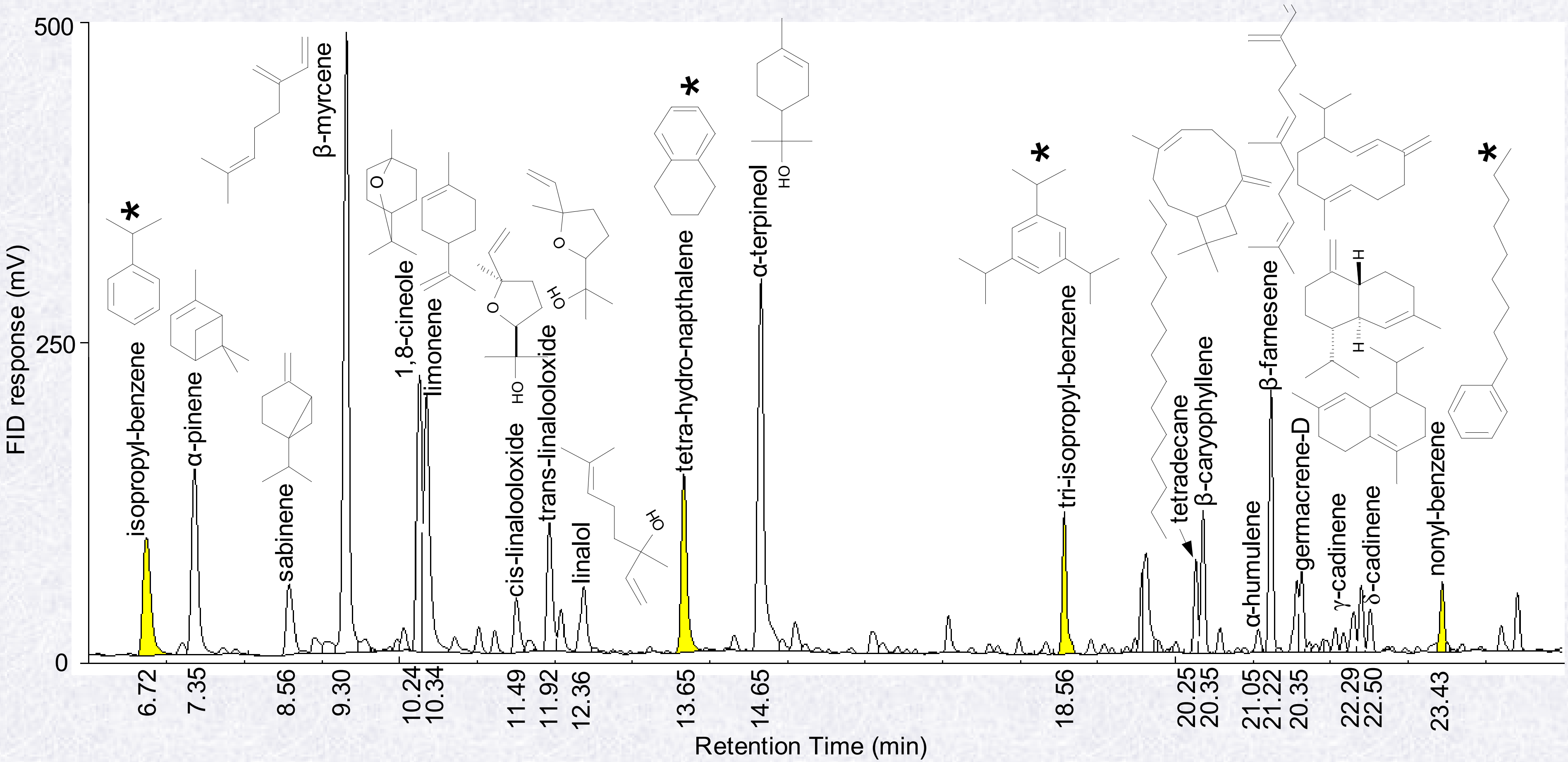


Measurement of SQT and MT emissions

- 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

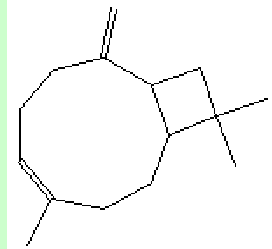


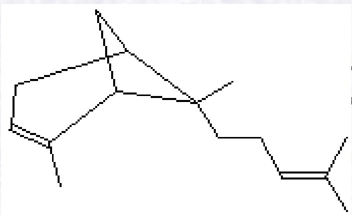
Chromatogram (plotted as the flame ionization detector (FID) response) from a ponderosa pine emission sample. Monoterpene retention times 7.2–14.7 min; sesquiterpene retention times 18.9-22.5 min. Shaded peaks are the aromatic compounds from the reference standard.

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

Prominent Sesquiterpenes in Recent Measurements

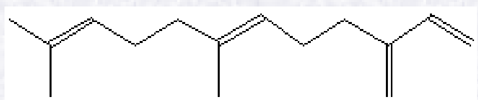
1. β-Caryophyllene

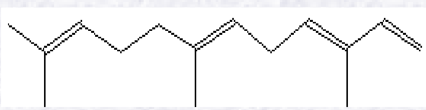




2. α/β- Bergamotene

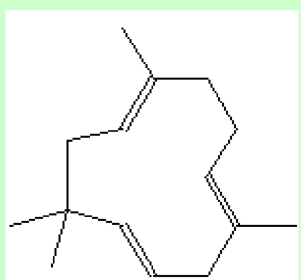
3. β-Farnescene



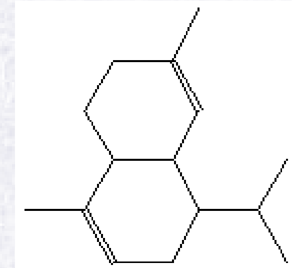


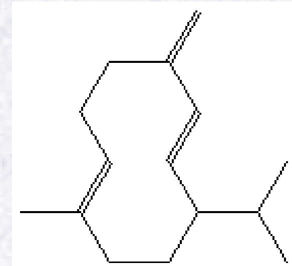
4. α-Farnescene

5. α-Humulene



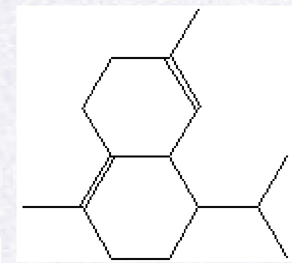
6. α-Muurolene

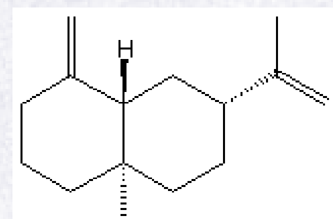




7. Germacrene D

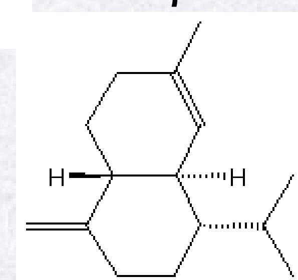
8. Δ-Cadinene





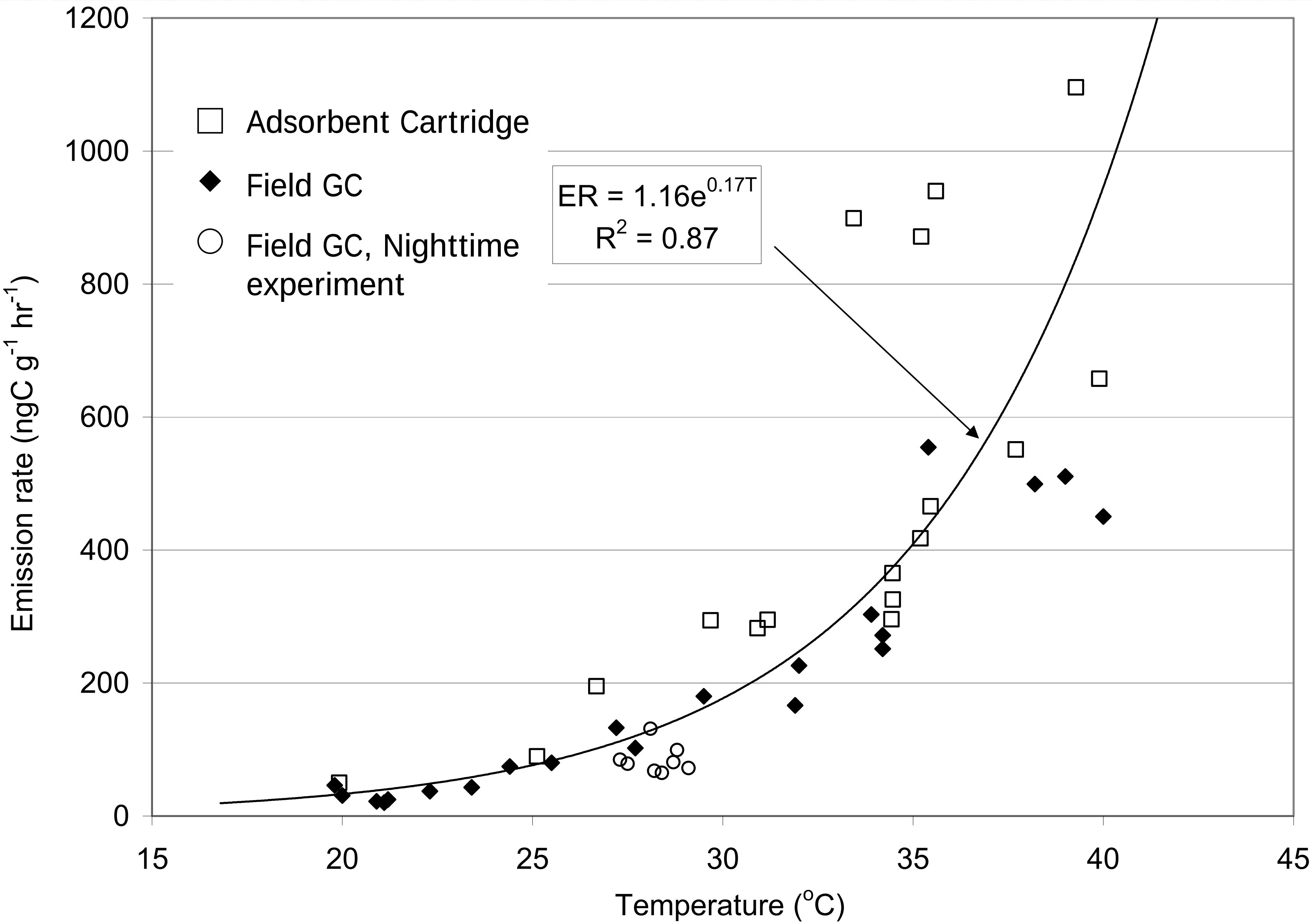
9. β-Selinene

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

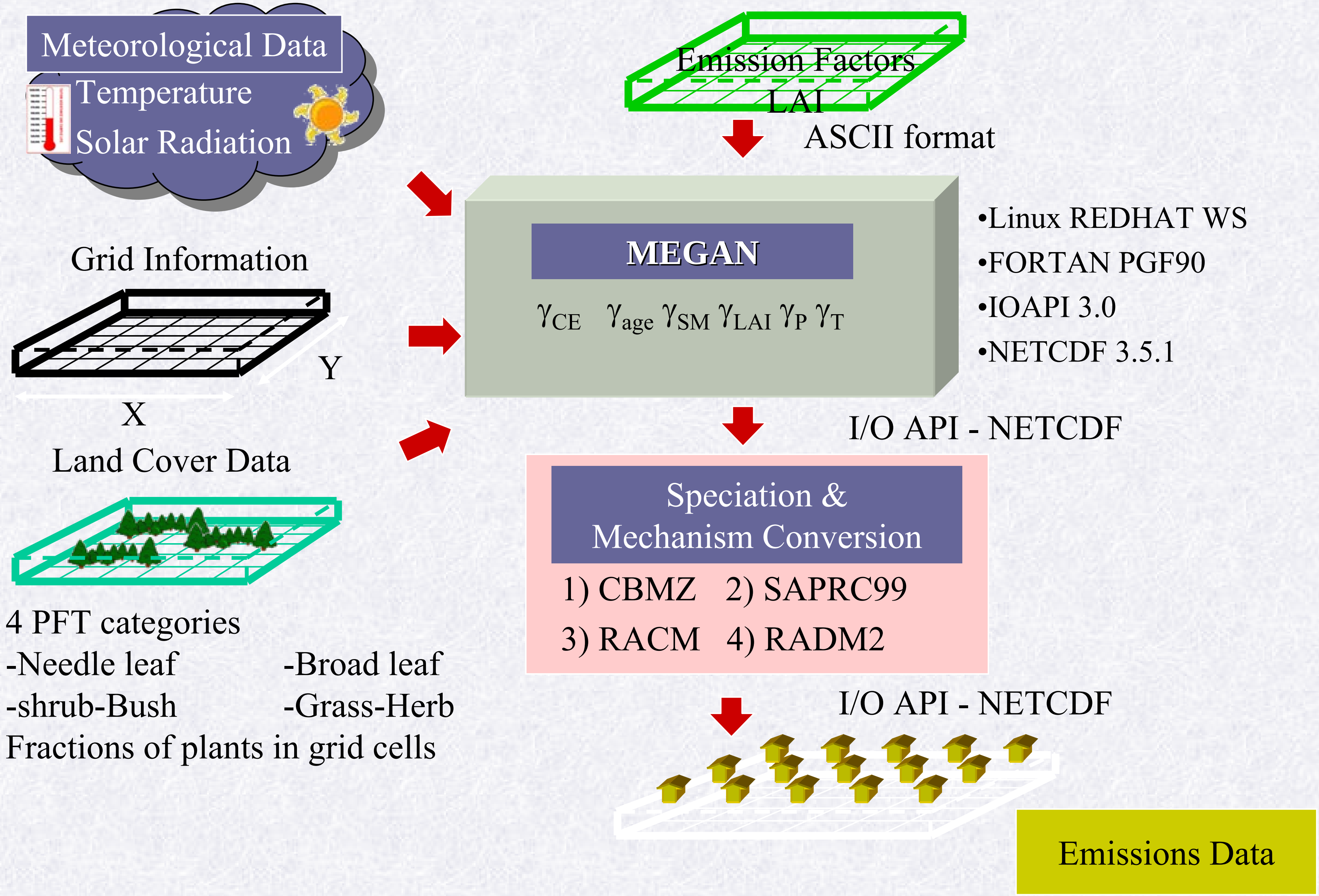
$$EM = \varepsilon \bullet \gamma_{CE} \bullet \gamma_{age} \bullet \gamma_{SM} \bullet \rho$$

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

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

Guenther, 2006

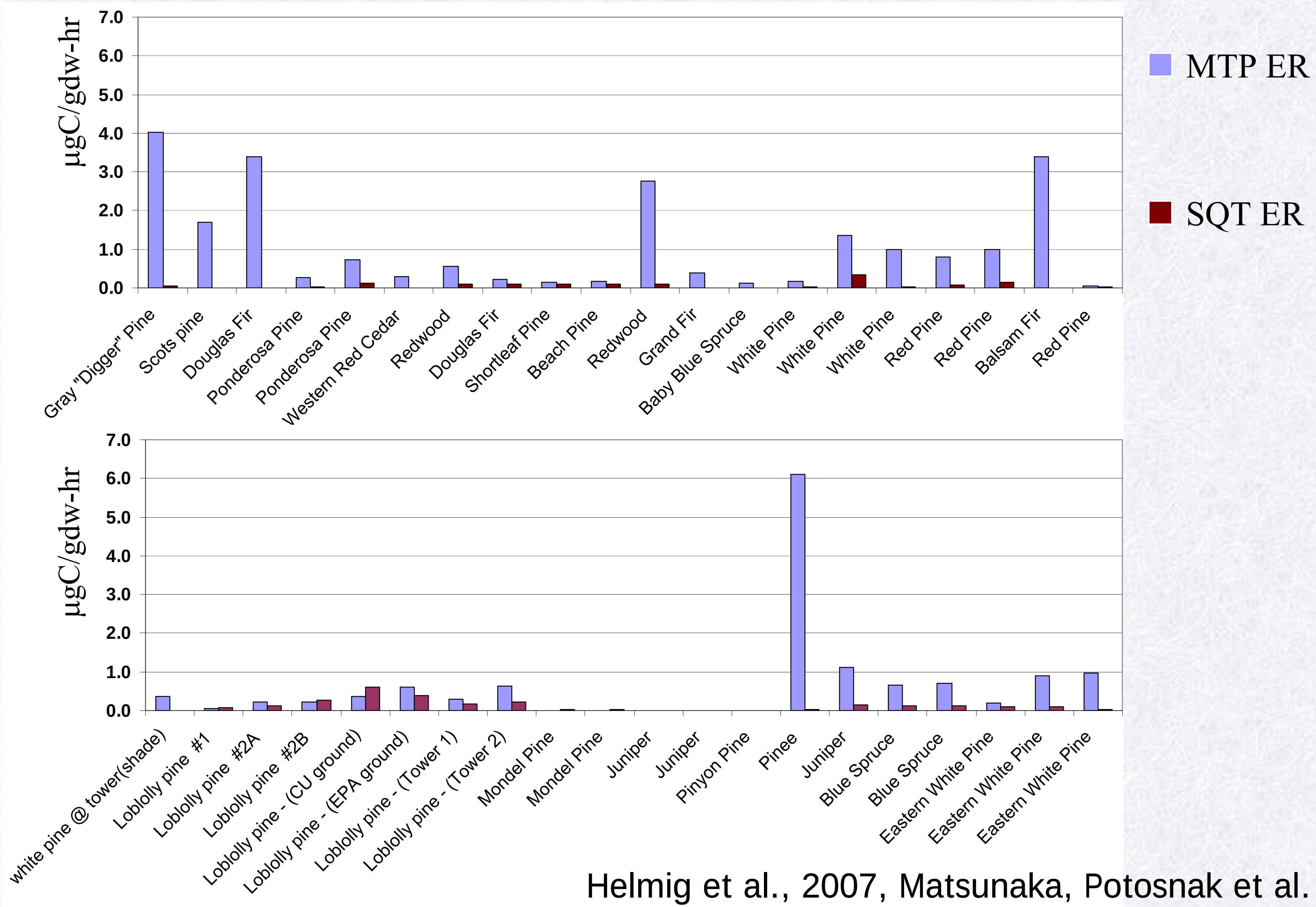
MEGAN v2.0


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

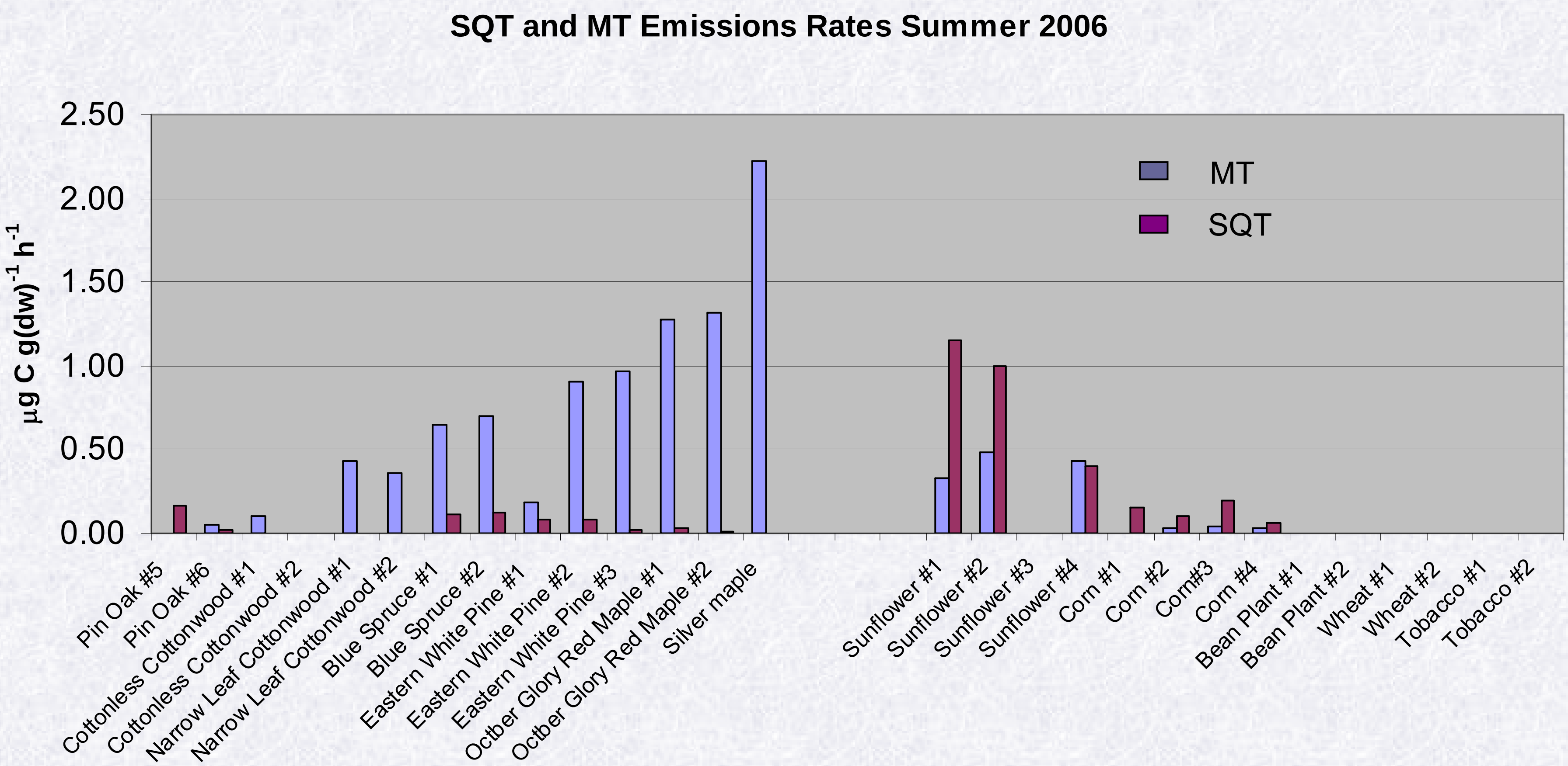
MEGAN v. BEIS3

- 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

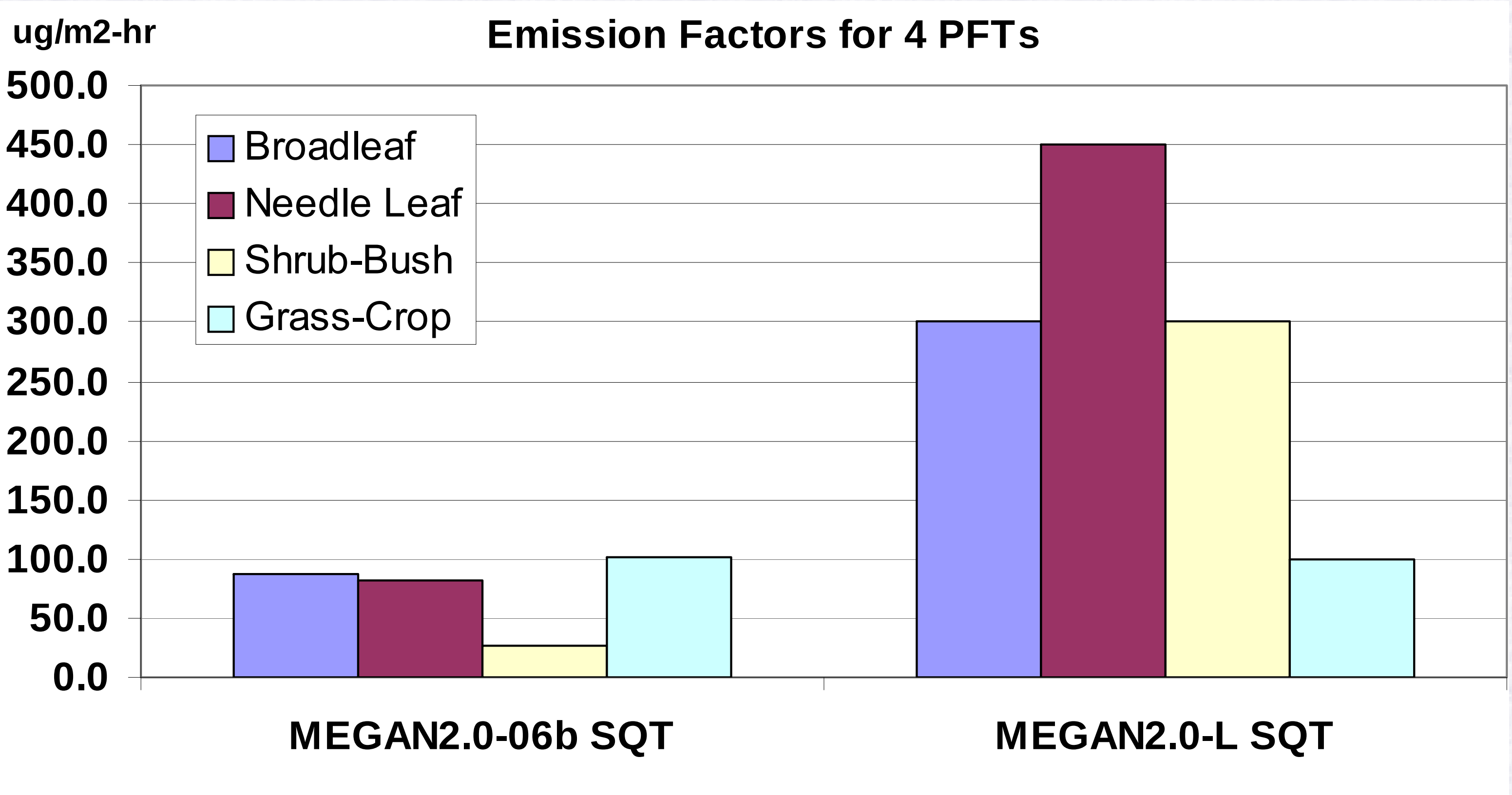
Helmig and Daly, 2007

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

Participants	Affiliation	Sample Collection	Analysis
Detlev Helmig	CU/INSTAAR	On-line On-line Tenax adsorbent	GC-MS GC-FID 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 Canisters	GC-MS GC-MS; GC-FID
Chris Geron Bob Arnts	USEPA	Tenax adsorbent	GC-MS
Hannele Hakola	Finnish Meteor. Institute	Tenax adsorbent	GC-FID

Courtesy of P. Harley

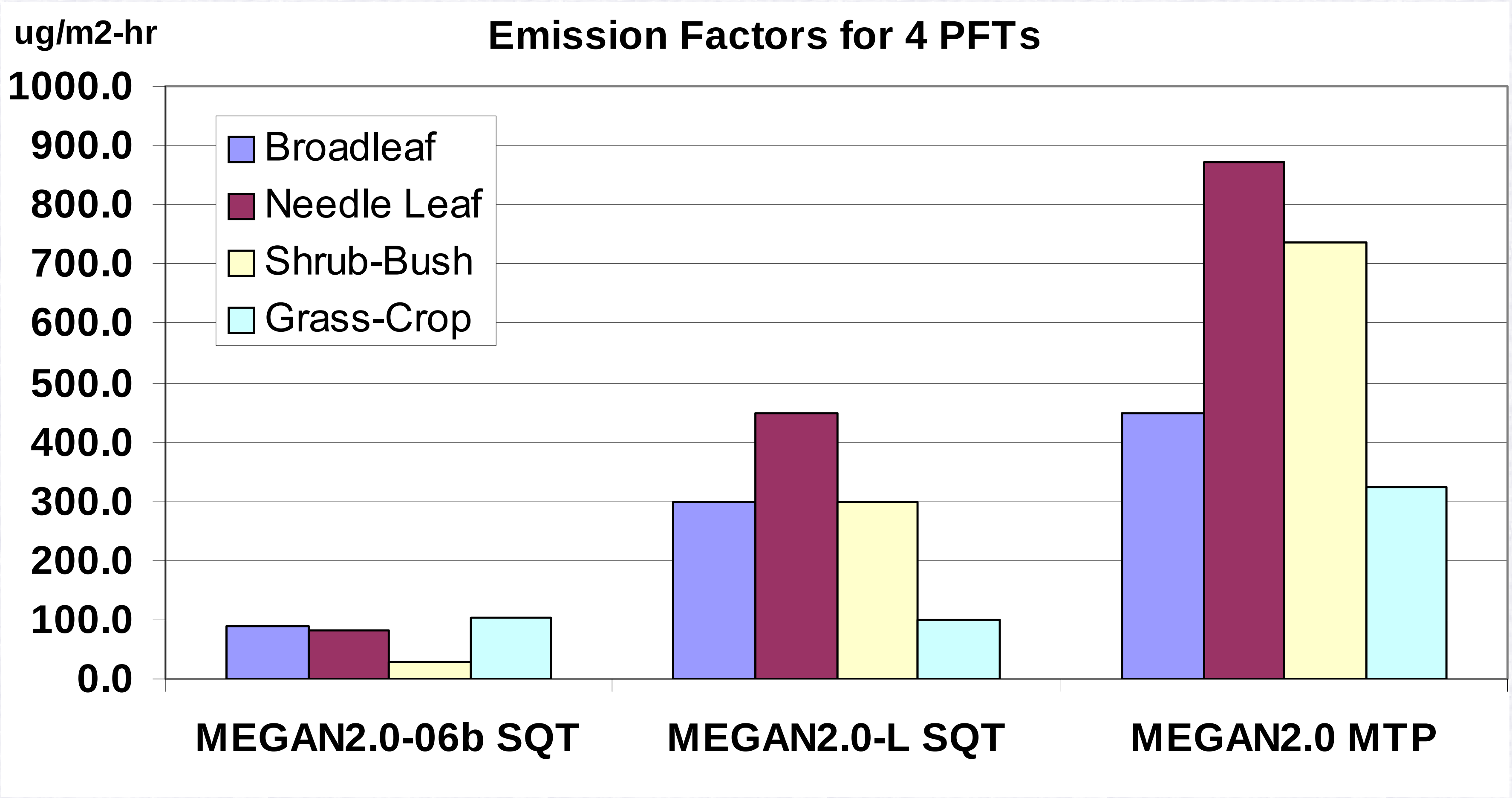
Comparison of SQT Emission Factors from Recent Measurements v. Prior Literature



Recent data

Literature through 2004

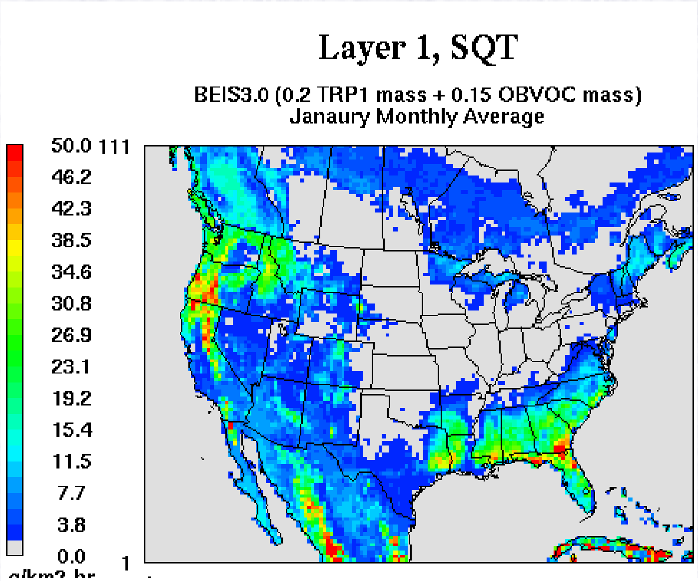
SQT and MT Emission Factors by Plant Functional Type

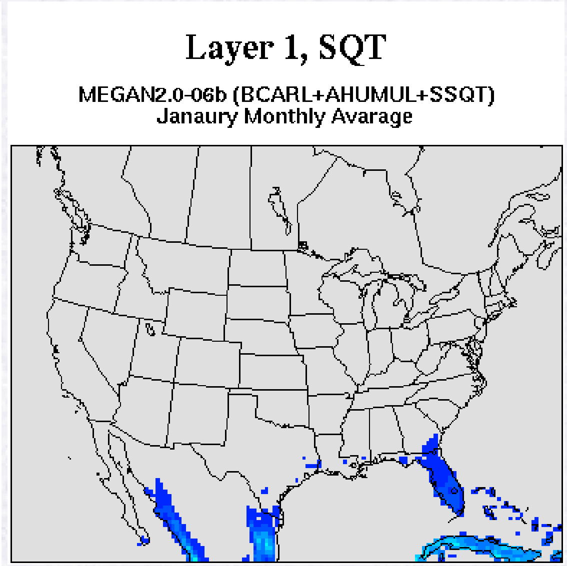


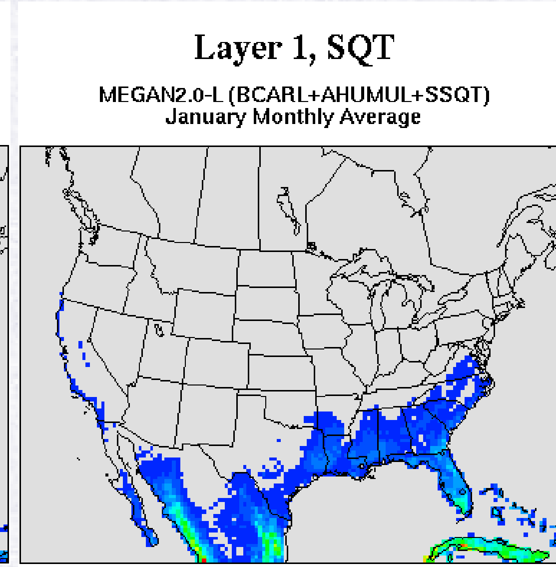
Recent data Literature through 2004 Recent data

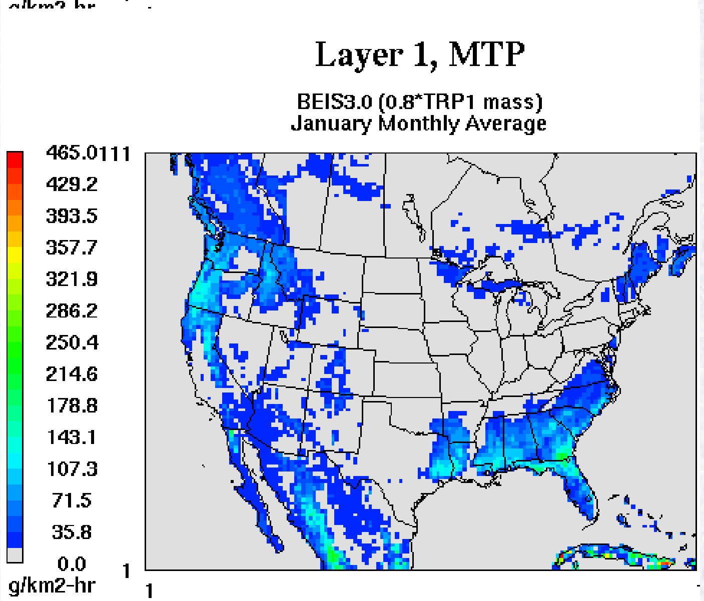
Emissions Modeling Results -- January

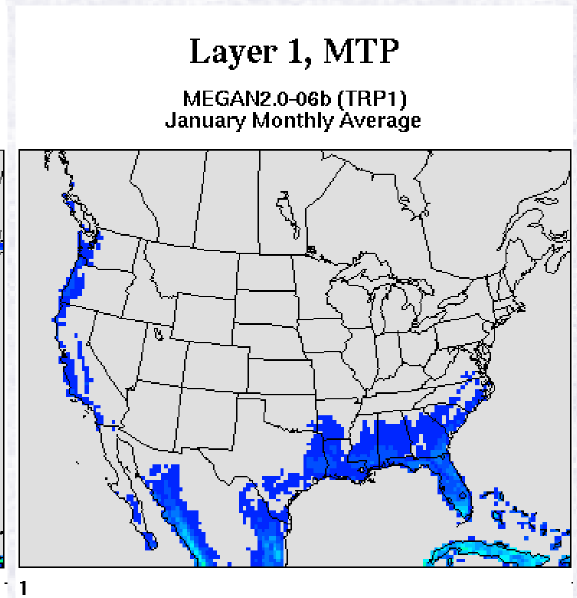
BEIS 3.0 | MEGAN2.0-06b | MEGAN2.0-L







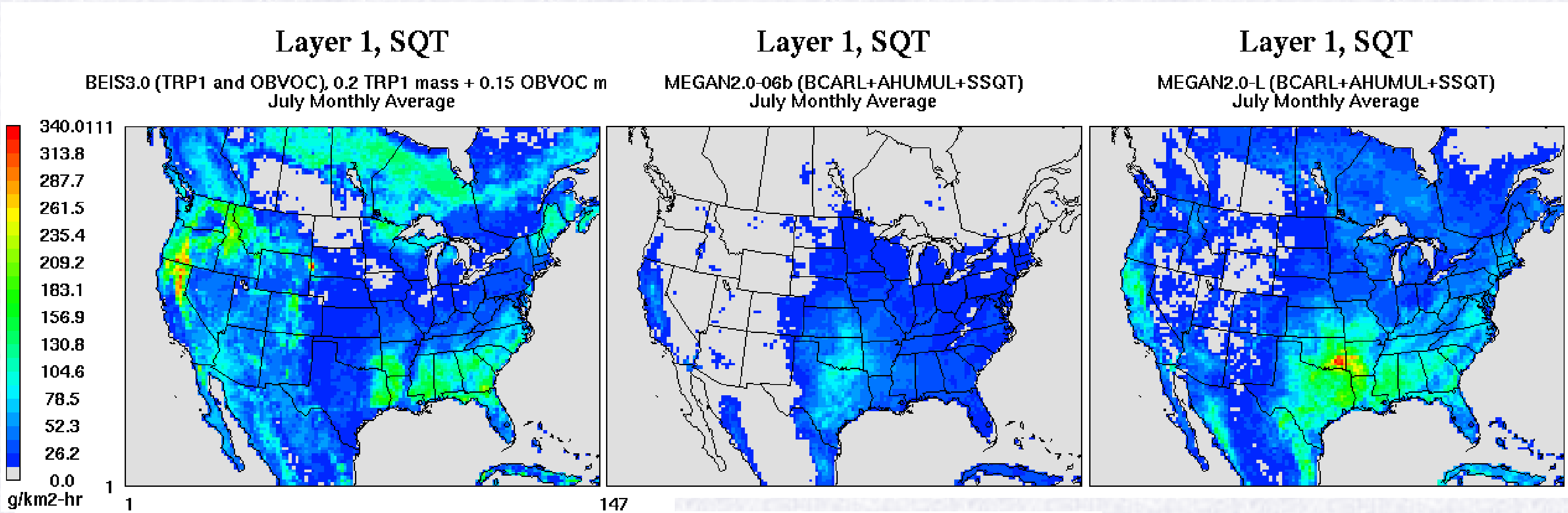


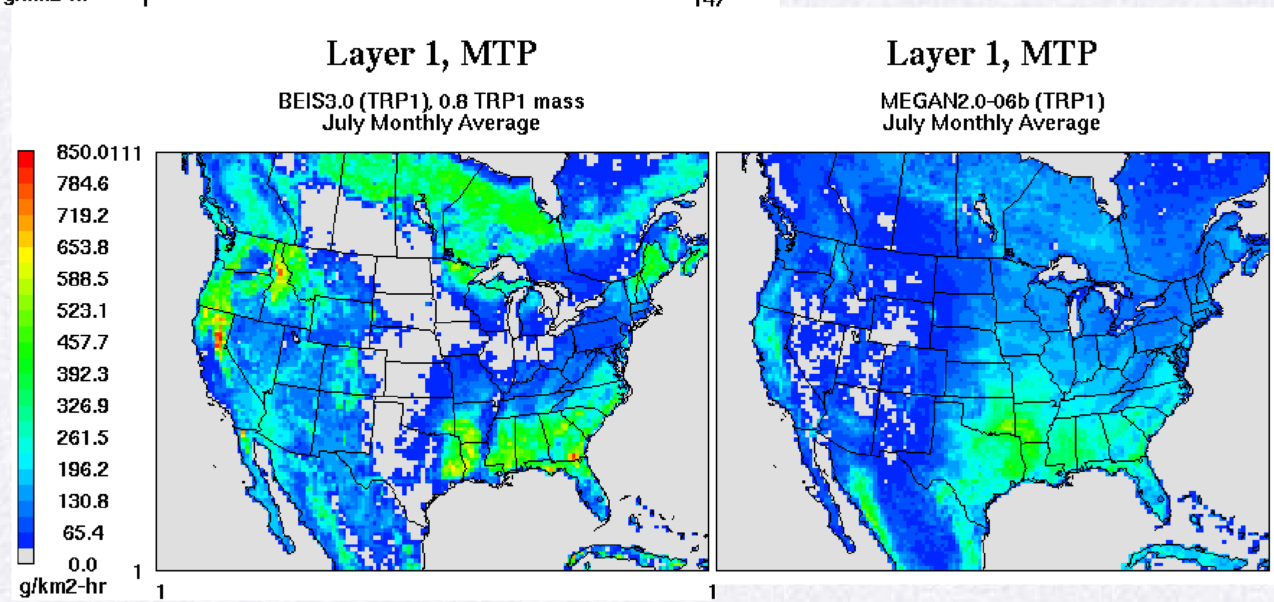


Max 465.8 g/km2-hr | Max 154.4 g/km2-hr | Max 154.4 g/km2-hr

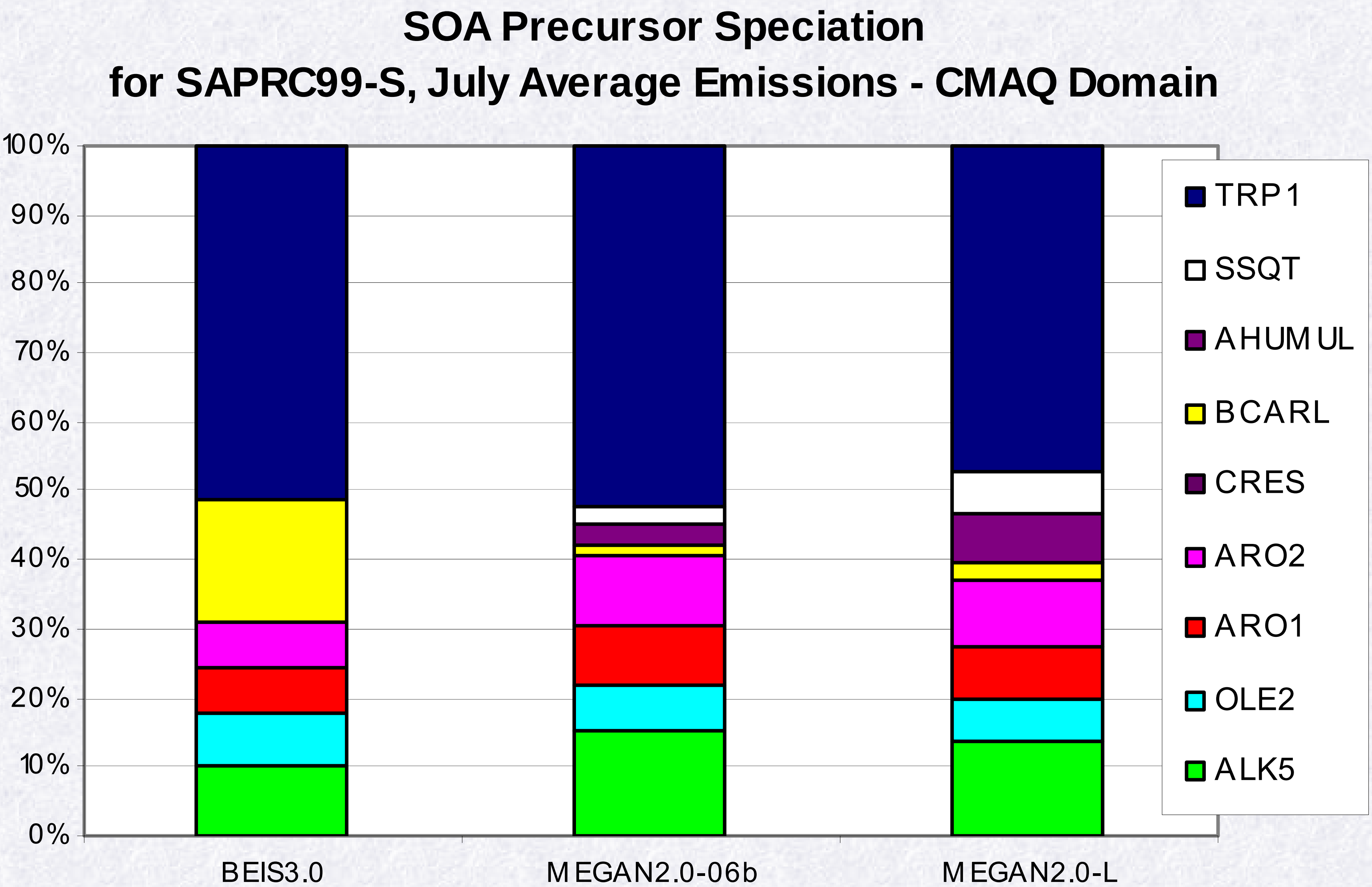
Emissions Modeling Results – July

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.