Modeling Atmospheric Chemistry and the Effect of Emissions from the Biosphere on Air Pollution and Climate

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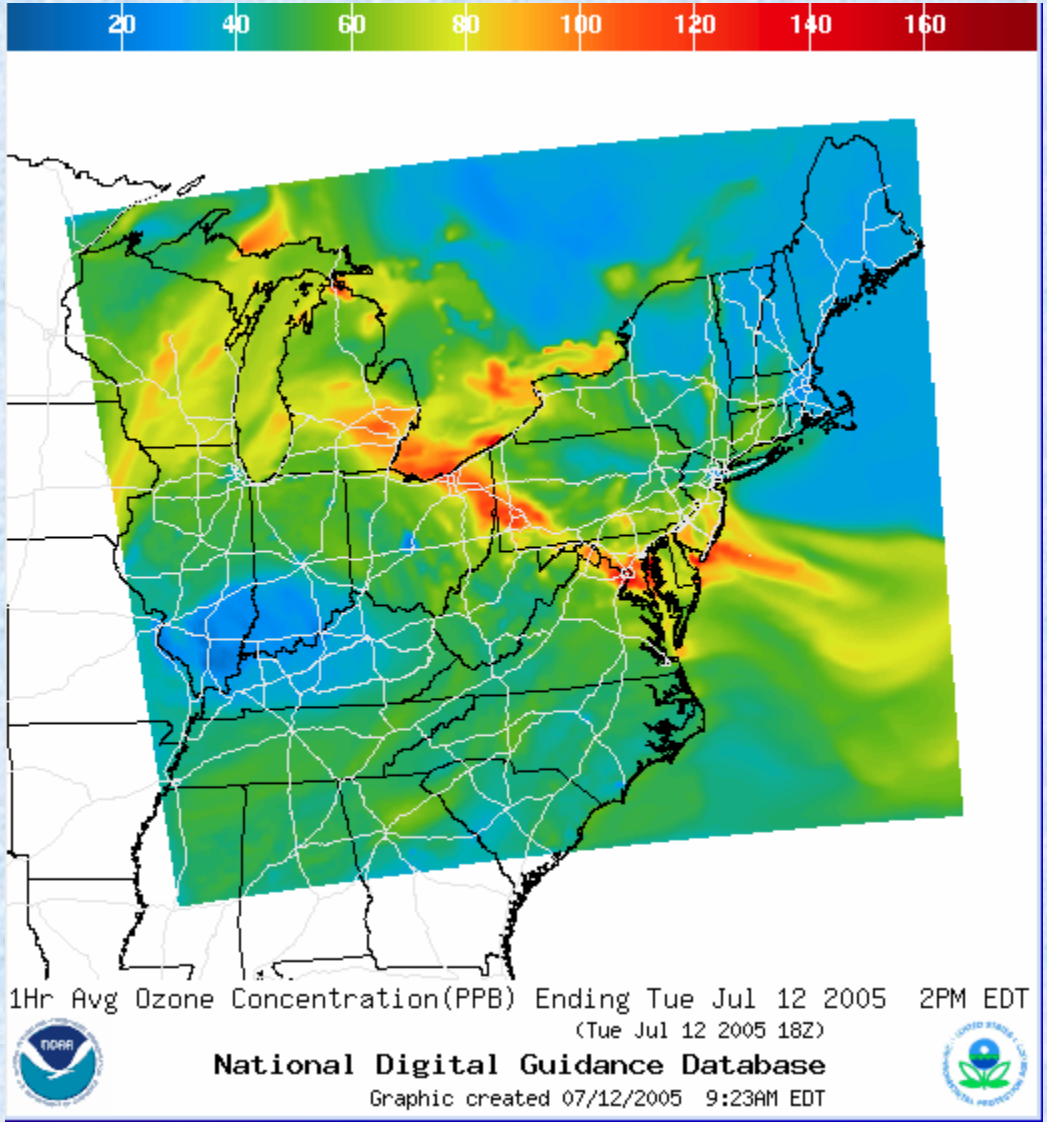
Air Quality Forecasting

Goal: To provide accurate and time-resolved 4-day forecasts of ozone, PM2.5 and visibility.



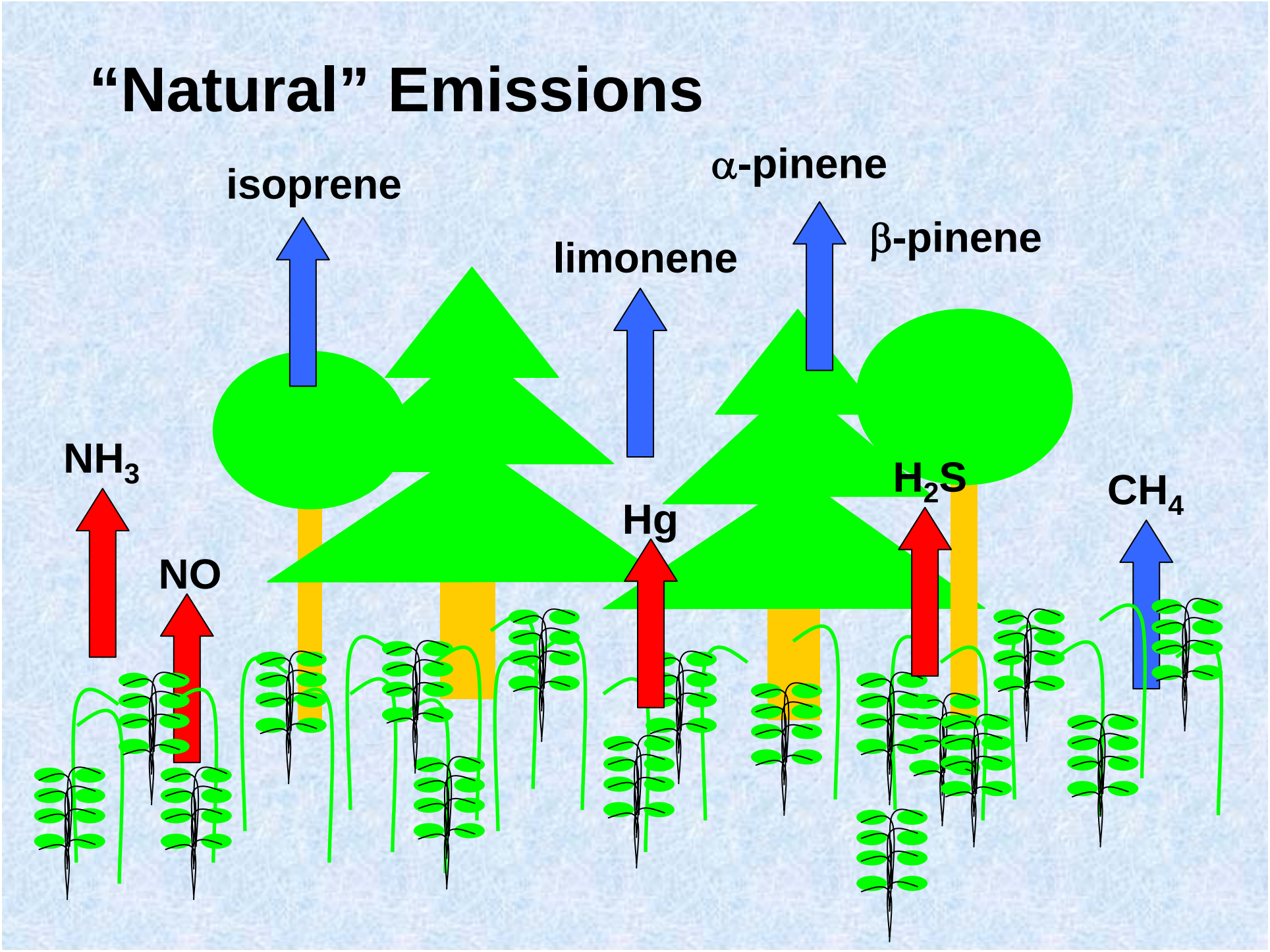
Health Effects of Air Pollution

- **More than 100 million individuals living in 114 different areas of the country are exposed to levels of air pollution that exceed one or more health-based ambient standards (U.S. EPA AIRS).**

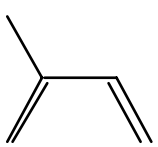
- **Exposure to high levels of particulate matter (PM) alone was responsible for up to 60,000 deaths each year in the U.S. (Kaiser, 2000, Health Effects Institute).**

- **Furthermore, PM10 (particles with aerodynamic diameters <10 μm) concentrations of 50 mg m^{-3} in the air results in a 5% increase in daily mortality and a 12% increase in hospital admissions (Dr. Dieter Schwela; World Health Organization).**

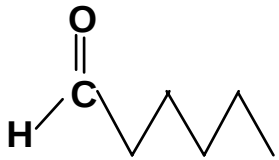
“Natural” Emissions



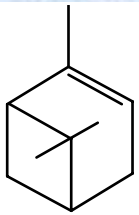
Biogenic Compounds



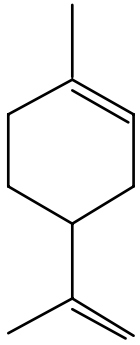
Isoprene



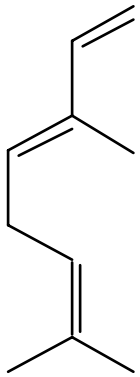
n-Hexanal



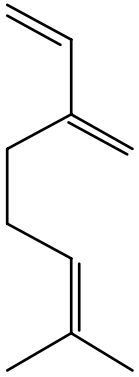
α-Pinene



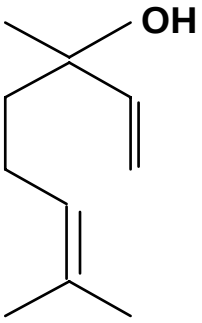
d-Limonene



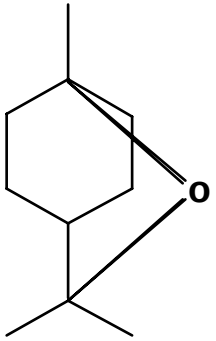
t-ß-Ocimene



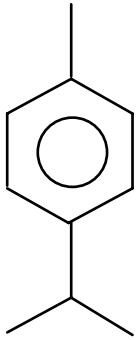
Myrcene



Linalool



1,8-Cineole



p-Cymene

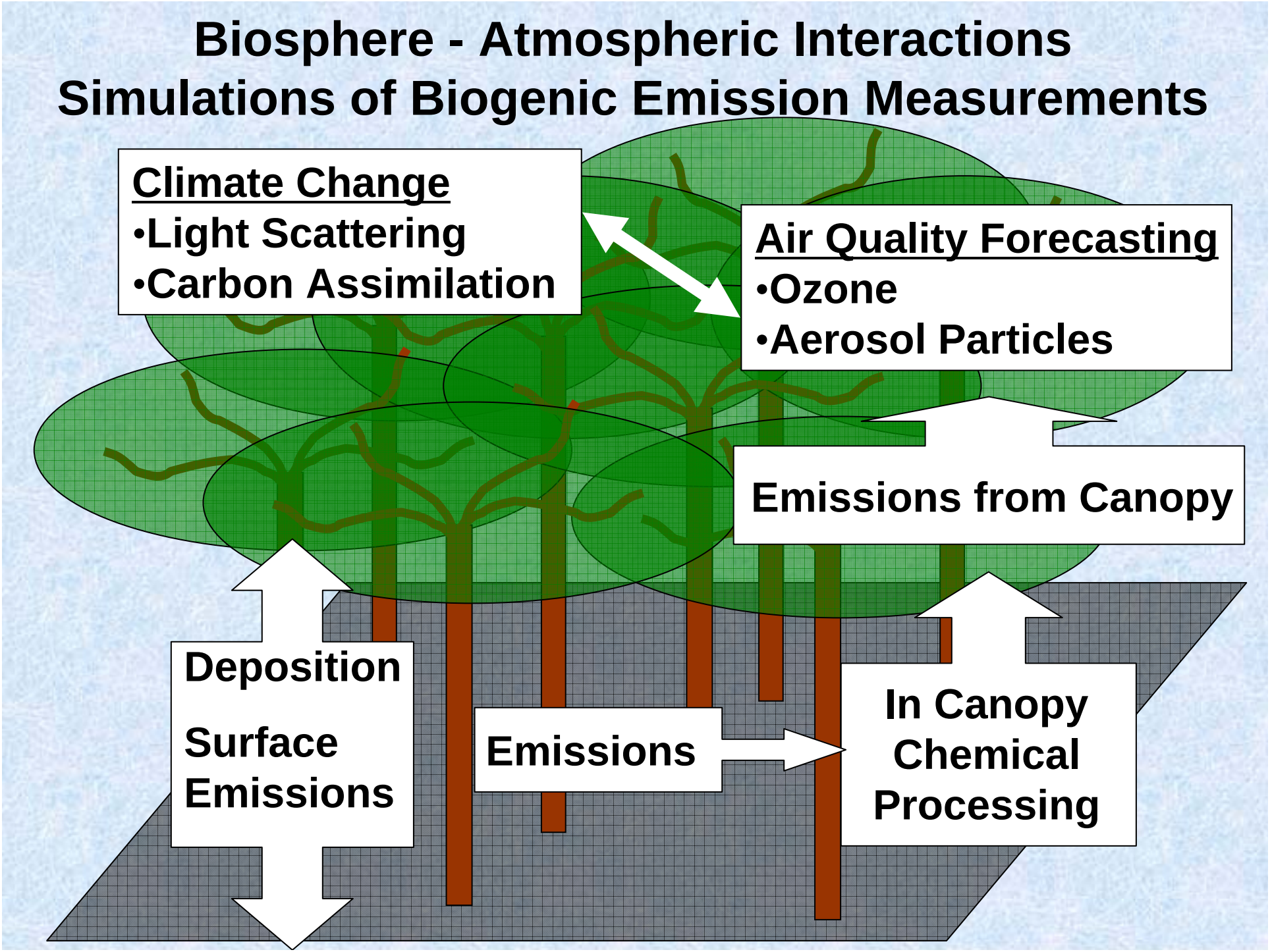
Lifetimes for BVOC Reactions

	HO	NO_3	O_3
isoprene	1.4 h	50 min	1.3 days
camphene	2.6 h	50 min	18 days
3-carene	1.6 h	4 min	11 h
limonene	50 min	3 min	2.0 h
myrcene	40 min	3 min	50 min
α-pinene	2.6 h	5 min	4.6 h
β-pinene	1.8 h	13 min	1.1 days

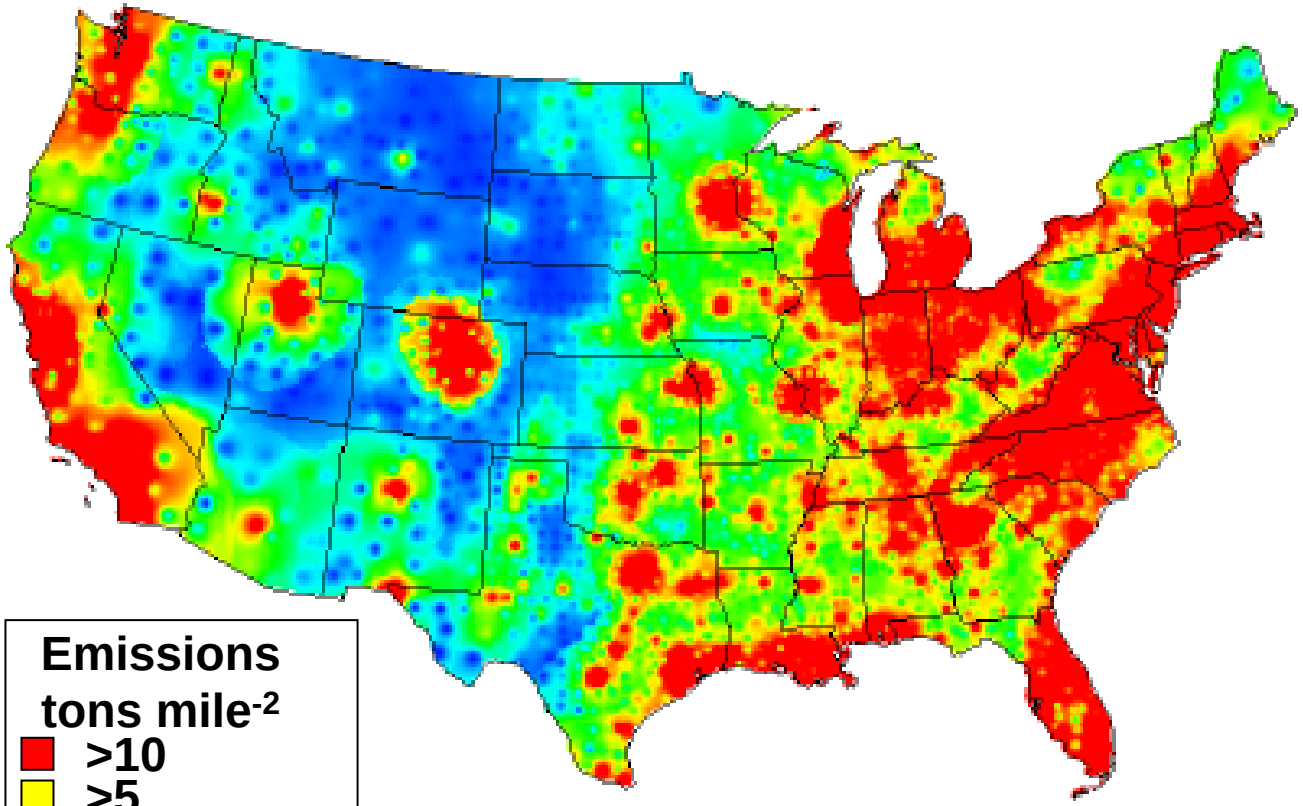
With concentrations (molecule per cubic centimeter) of HO, 12-h daytime average of 2.0×10^6 ; NO_3 , 12-h nighttime average of 5×10^8 ; O_3 , 24-h average of 7×10^{11}.

Fuentes et al. … Stockwell, *Bull. Amer. Meteor. Soc.*, *81*, 1537-1575, 2000.

Biosphere - Atmospheric Interactions
Simulations of Biogenic Emission Measurements

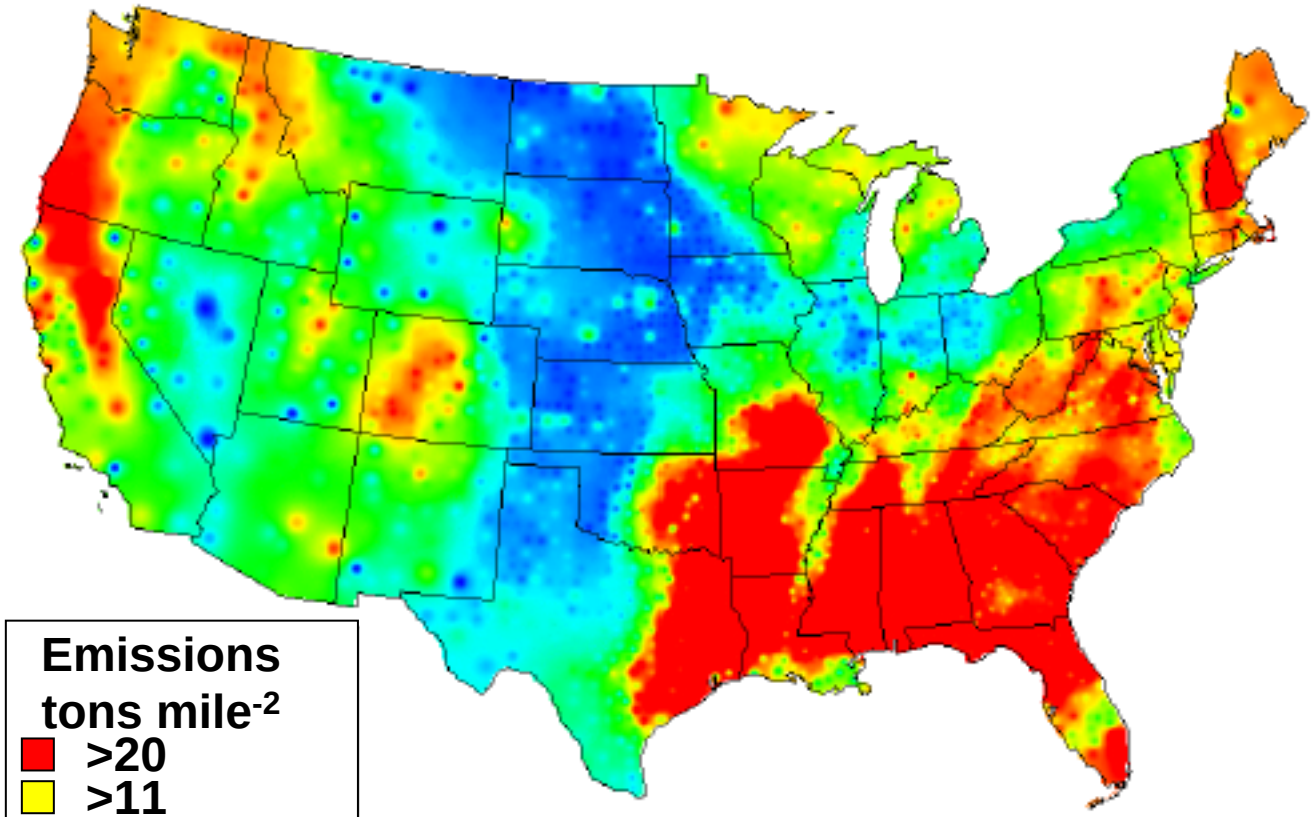


VOC Emissions



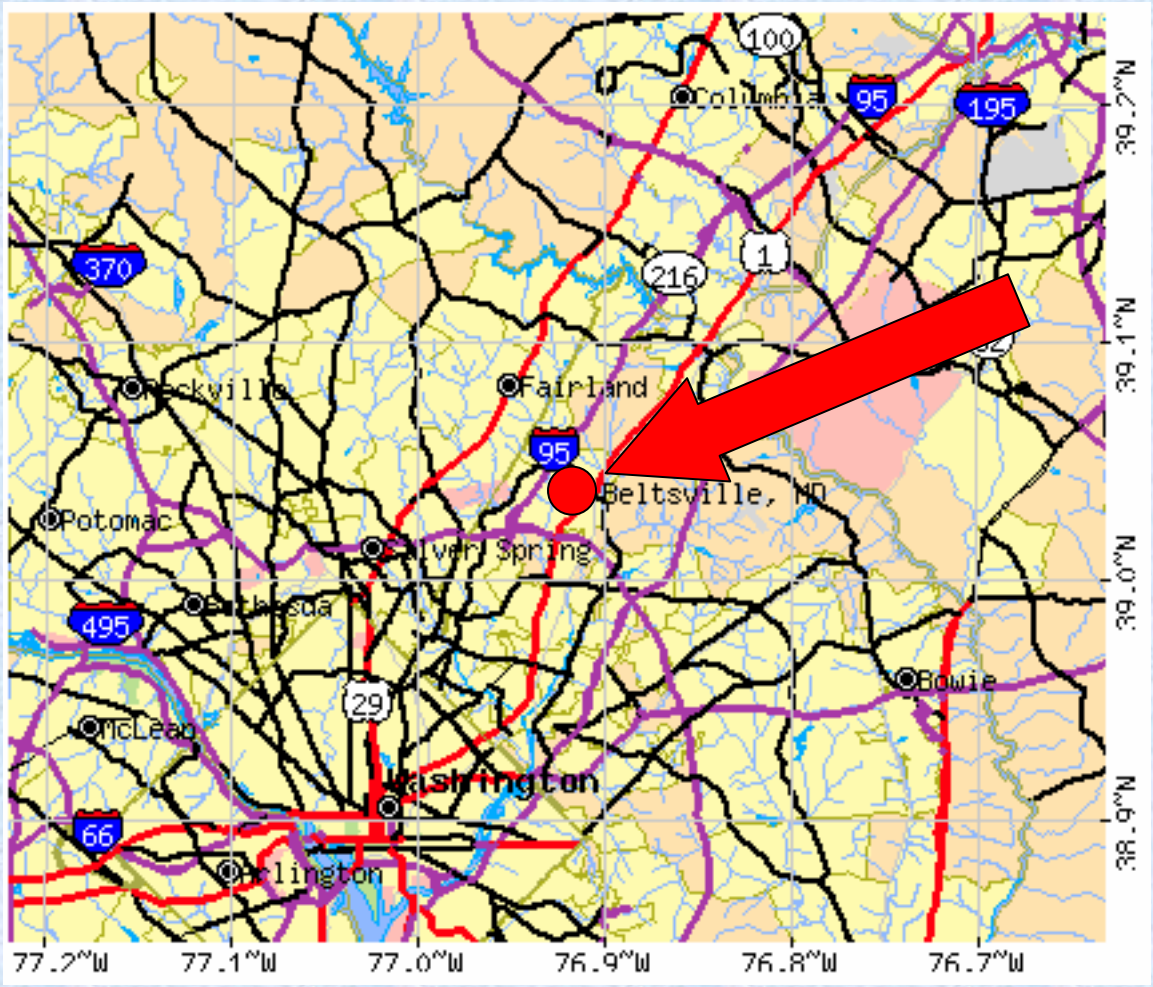
U.S. EPA

Biogenic VOC Emissions



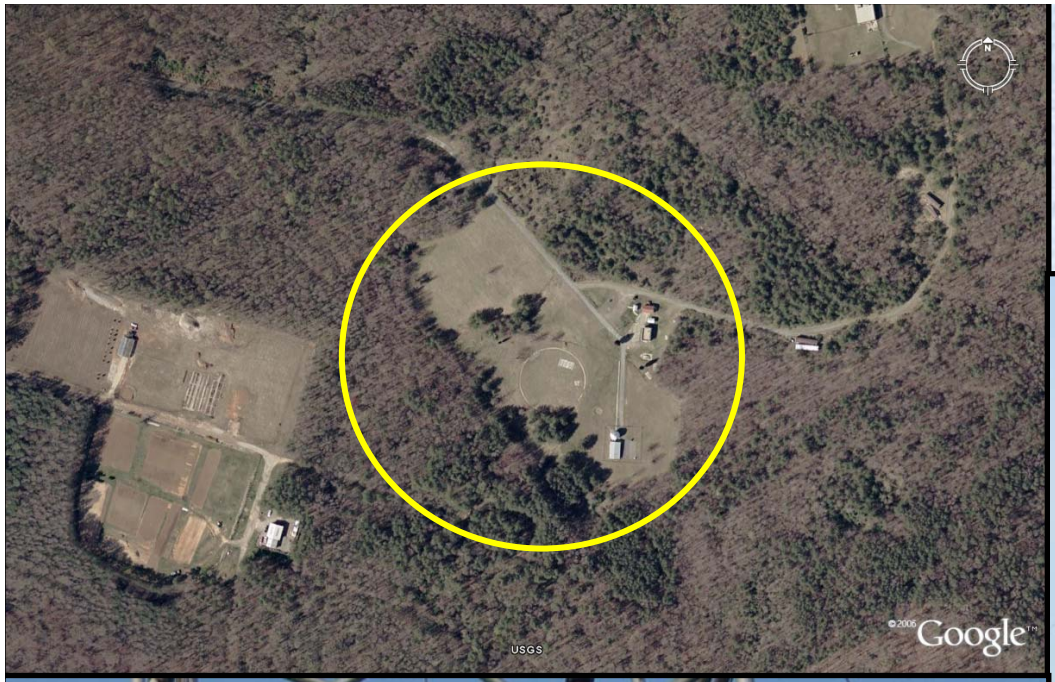
U.S. EPA

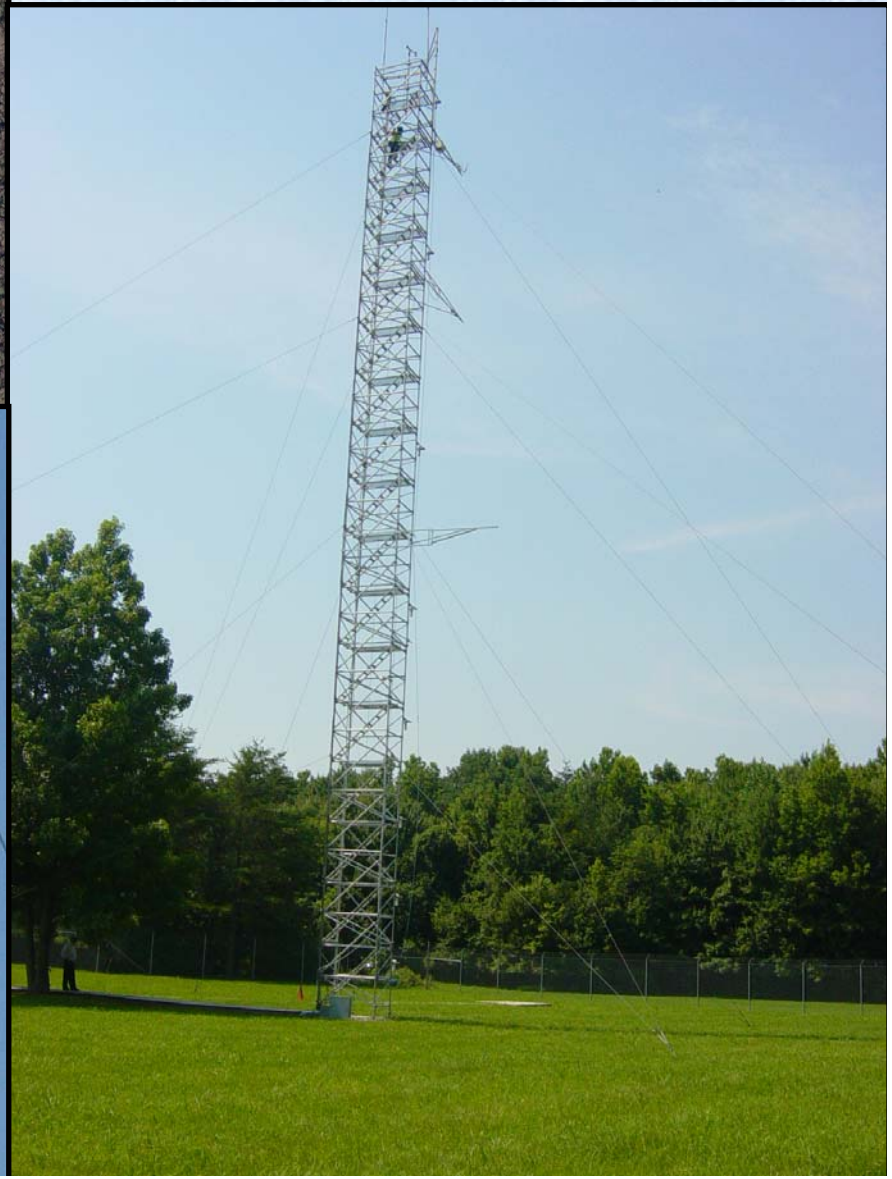
Beltsville Location



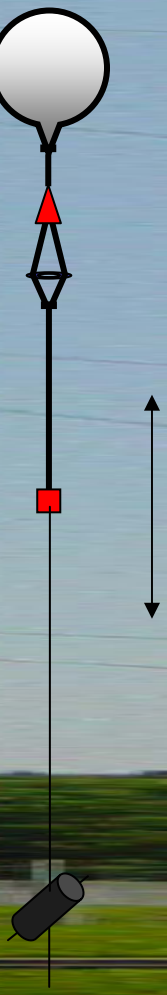
Howard University
Atmospheric Research Site

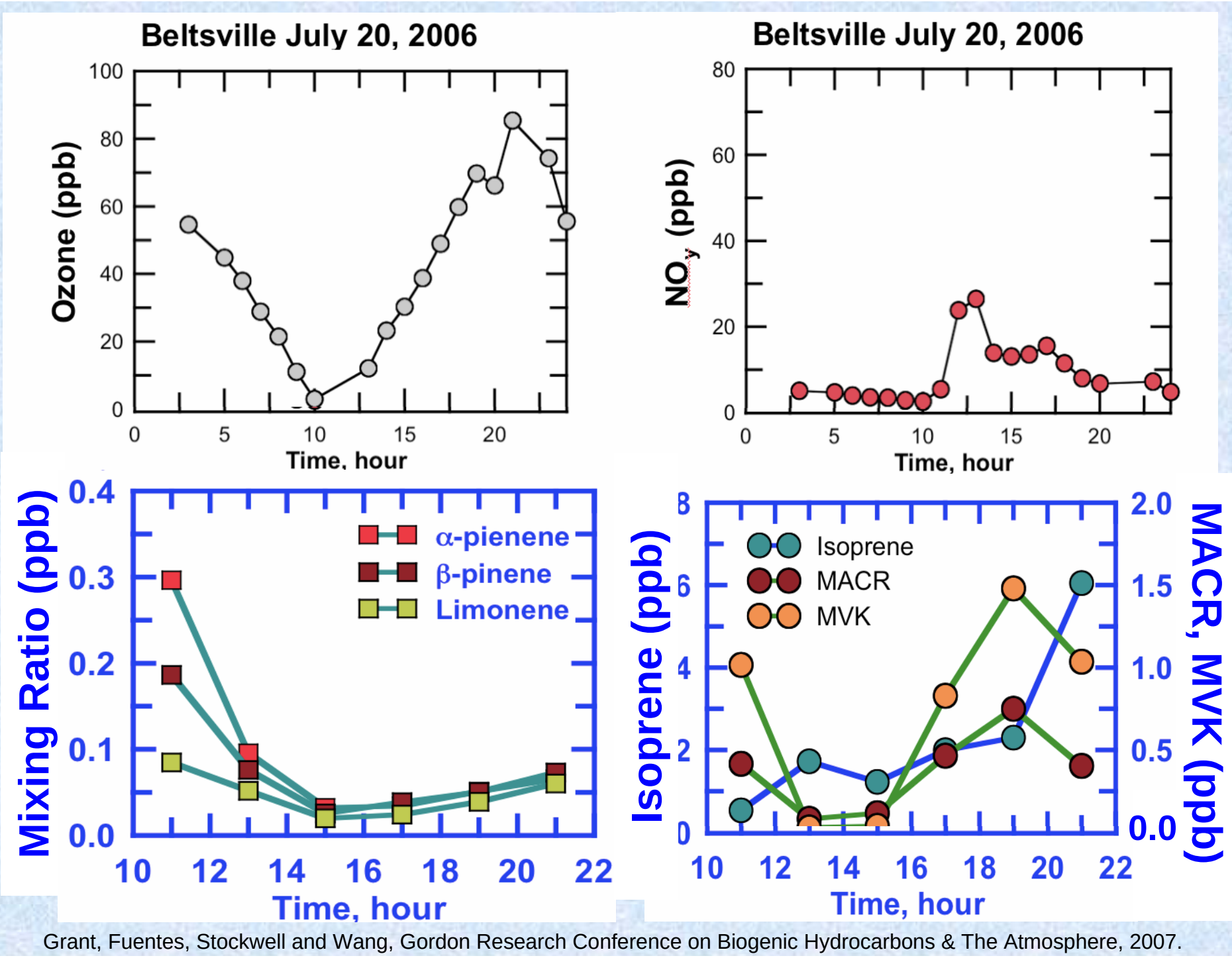
Beltsville, MD





Captive Ozonesonde

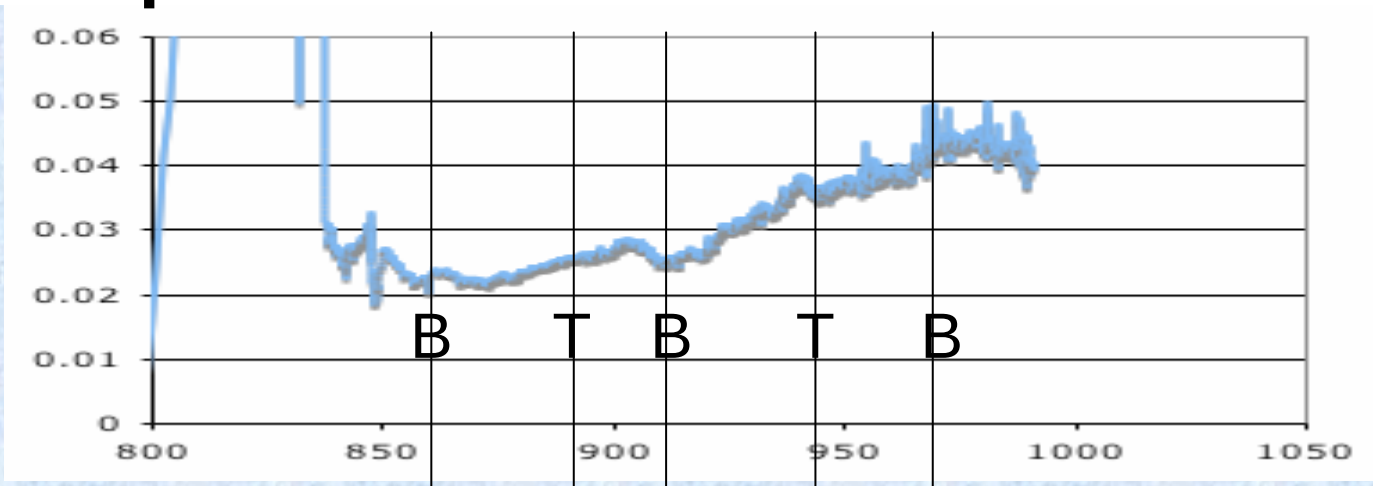




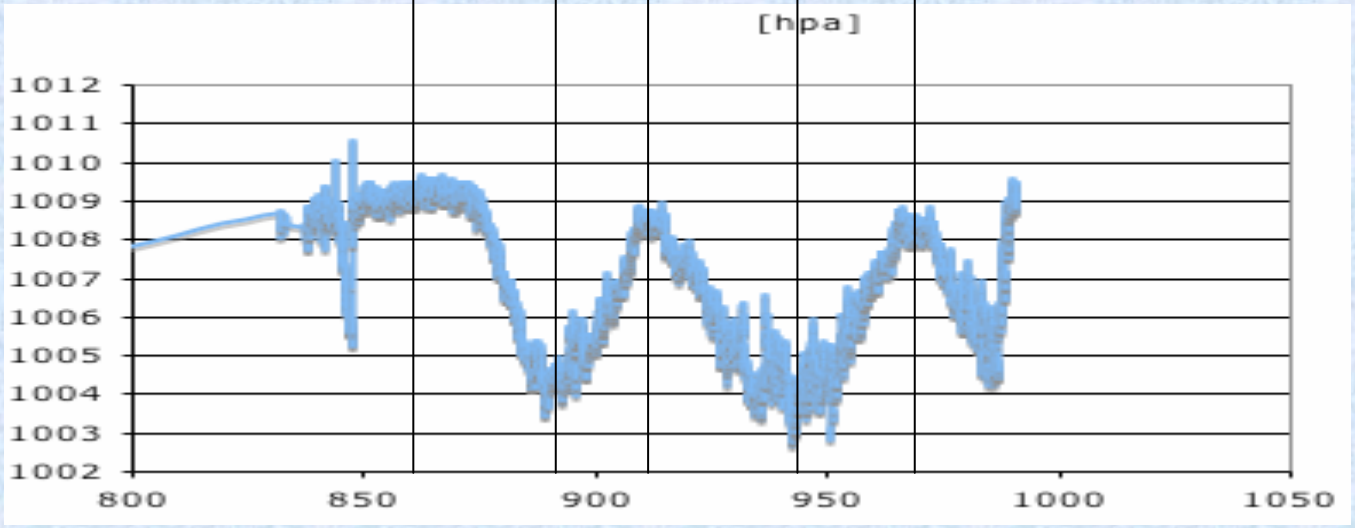
Grant, Fuentes, Stockwell and Wang, Gordon Research Conference on Biogenic Hydrocarbons & The Atmosphere, 2007.

Captive Ozonesonde Data

Ozone (ppm)



Pressure (mb)

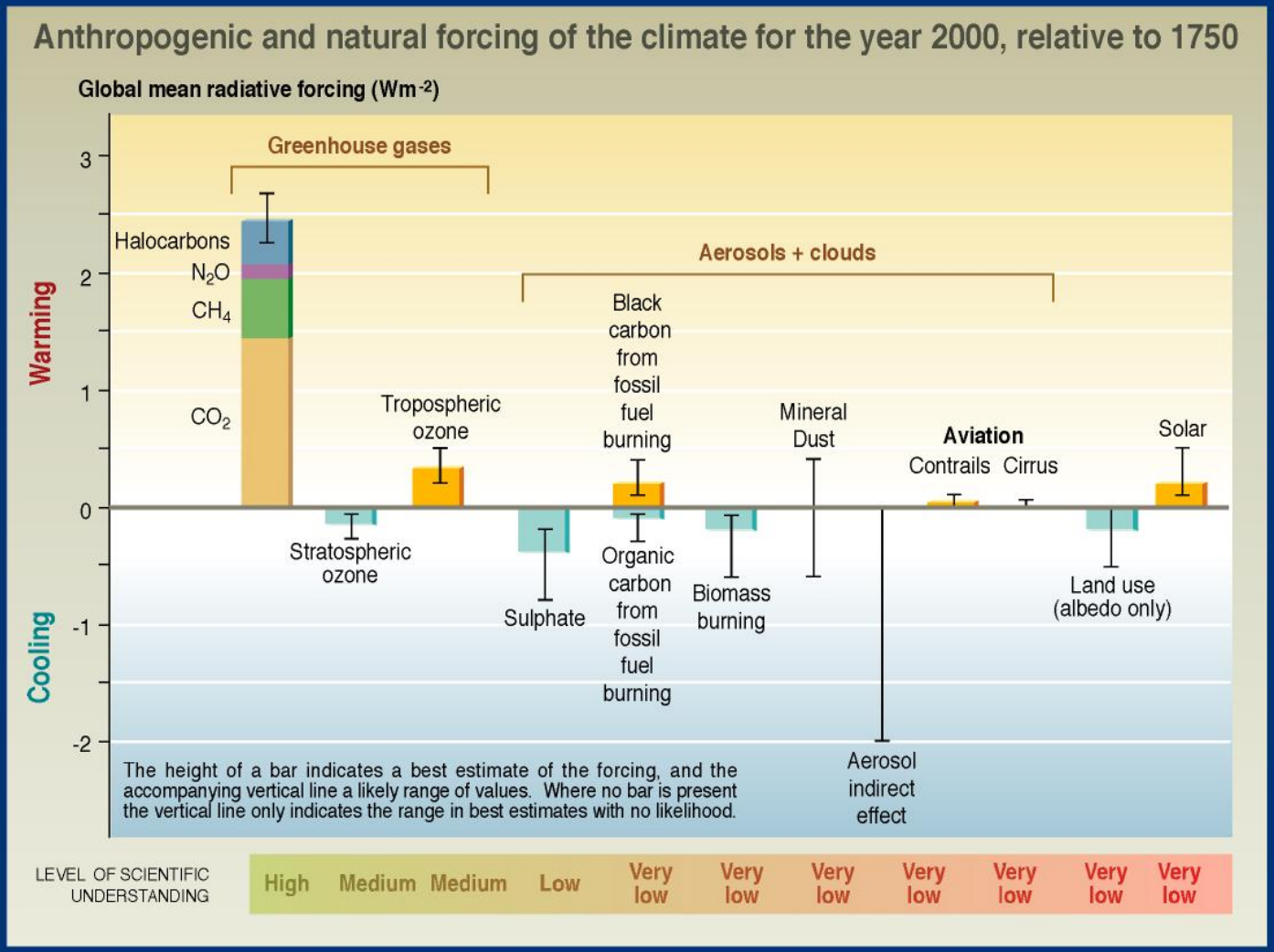


Time (min)

Work is in Progress to Understand These Field Measurements

Question 2: What are some of the consequences of this research?

Modeling of forest canopy processes is providing some answers.



SYR - FIGURE 2-2

IPCC | INTERGOVERNMENTAL PANEL ON CLIMATE CHANGE

WMO UNEP

http://www.ipcc.ch/present/graphics/2001syr/large/06.01.jpg

Simulation of Secondary Organic Aerosols in CMAQ

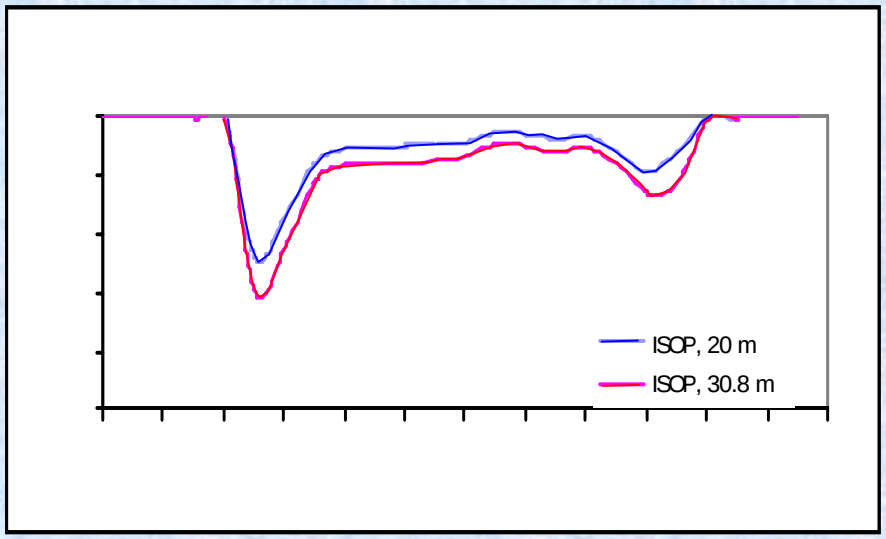
(Zhang et al., 2007, JGR 112, D20207, doi:10.1029/2007JD008675)

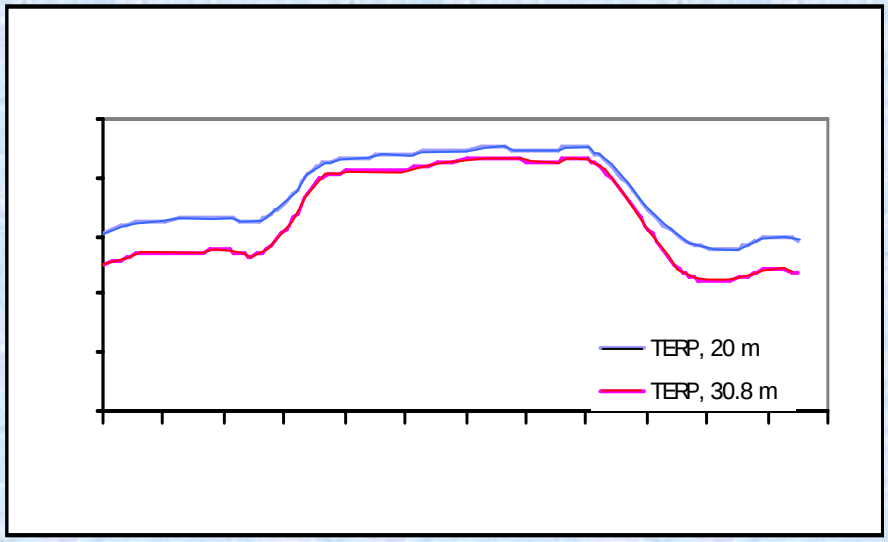
- **The default SOA module in CMAQ**
  - **Based on absorptive partitioning module of Schell et al. (2001)**
  - **It simulates SOA formation from 5 SVOCs (higher alkanes, xylene, cresole, tolueue, and terpenes)**
- **Two parameters needed for simulating SOA in CMAQ**
  - **The gas/particle partitioning coefficient, $K_{om,i}$**
  - **The stoichiometric coefficient, α_i**
- **SOA formation from isoprene photooxidation**
  - **Values of α_i and $K_{om,i}$ based on Caltech smog data at low NO_x conditions (Kroll et al., 2006; Henze and Seinfeld, 2006)**
  - **ISOP + OH $\rightarrow$ α_1 G_1 + α_2 G_2**

where G_1 and G_2 represent high and low SOA yield products

Simulation of Secondary Organic Aerosols in CMAQ (Stockwell, 2007)

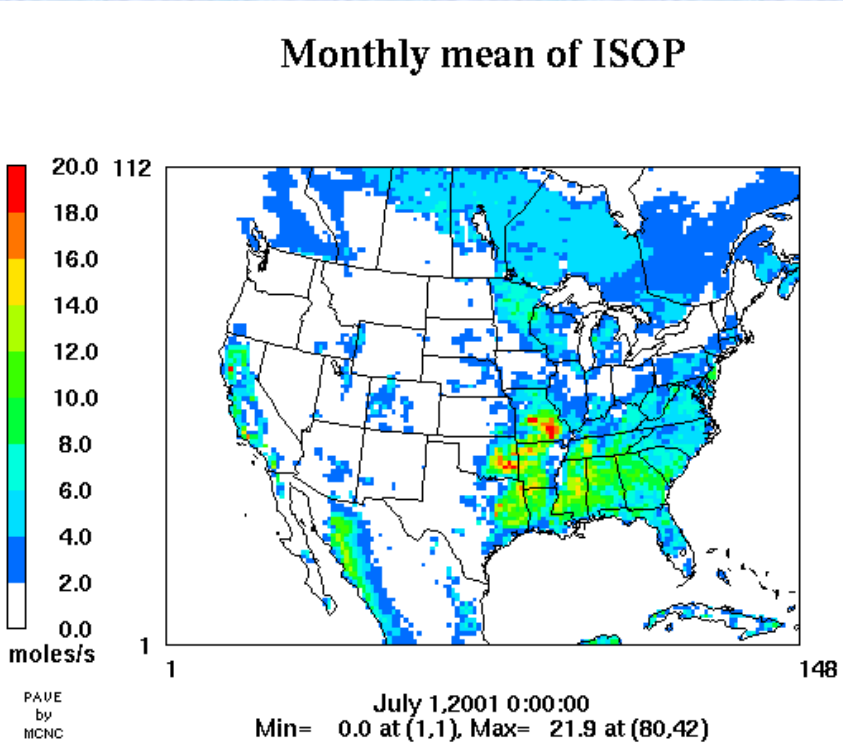
- **SOA formation from in-canopy reactions**
  - **Box model simulations were conducted assuming reactions occur (1) within canopy (0-20 m); (2) from surface to 10.8 km above the canopy (0-30.8 m).**
  - **The time-dependent emission adjustment factors for isopene and terpene were derived and applied for baseline emissions.**
  - **The reduced emissions are assumed to produce SOA precursors, ISOPAER and TERPAER, respectively.**



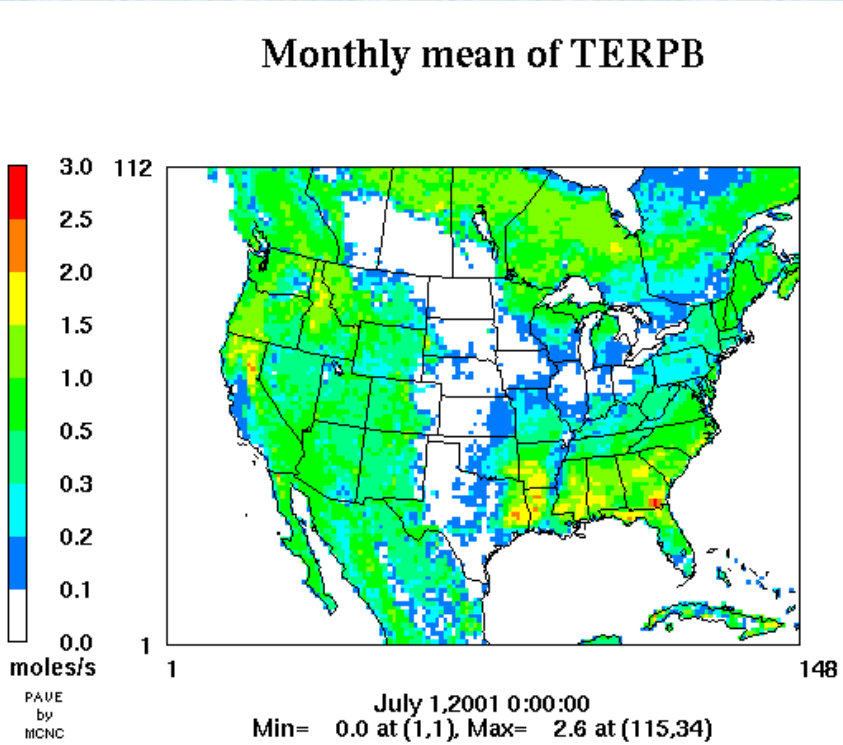


Monthly-Mean Emissions

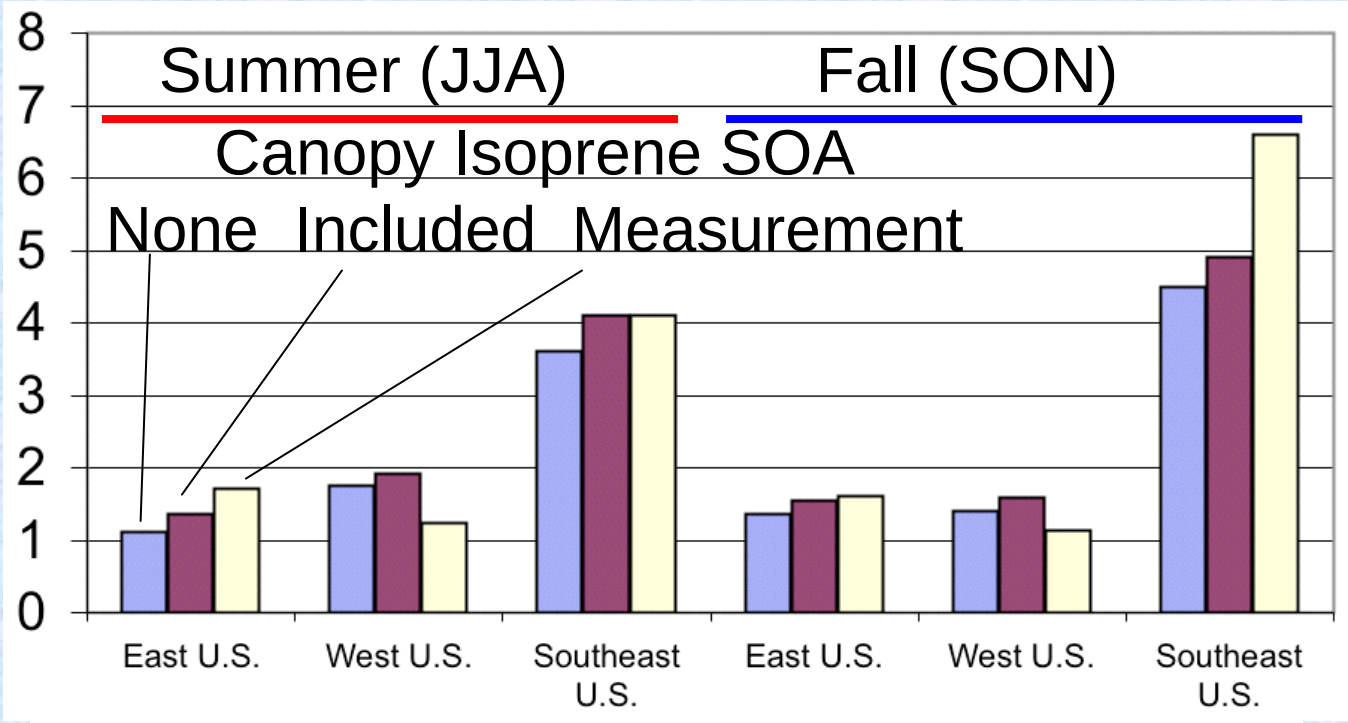
Isoprene

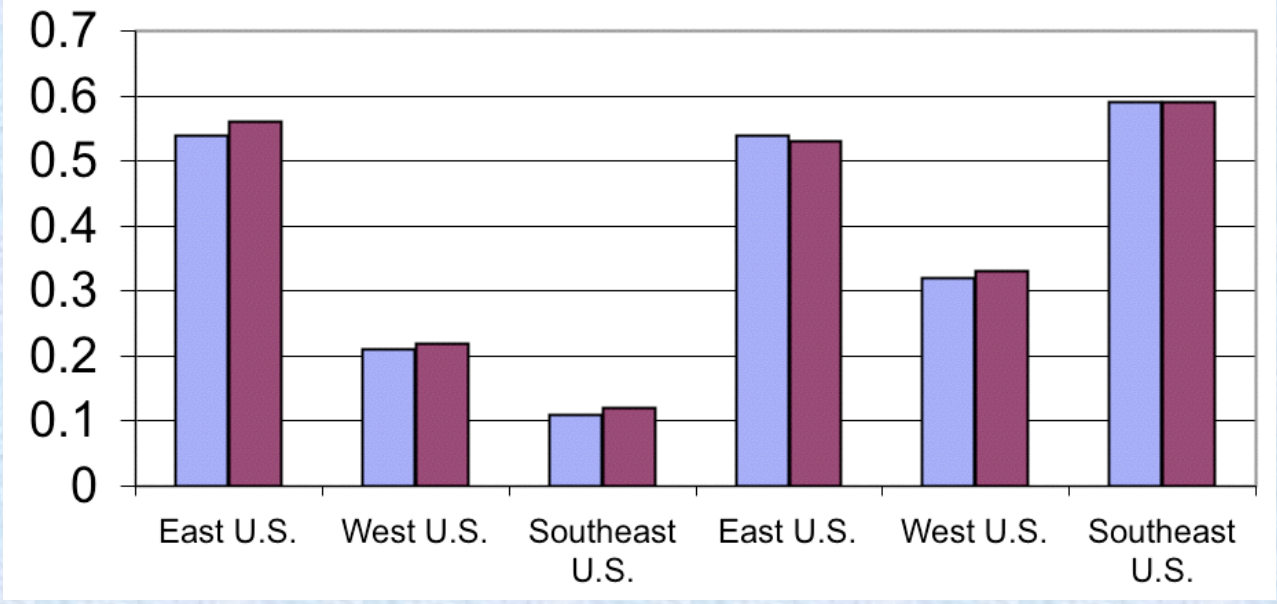


Terpene



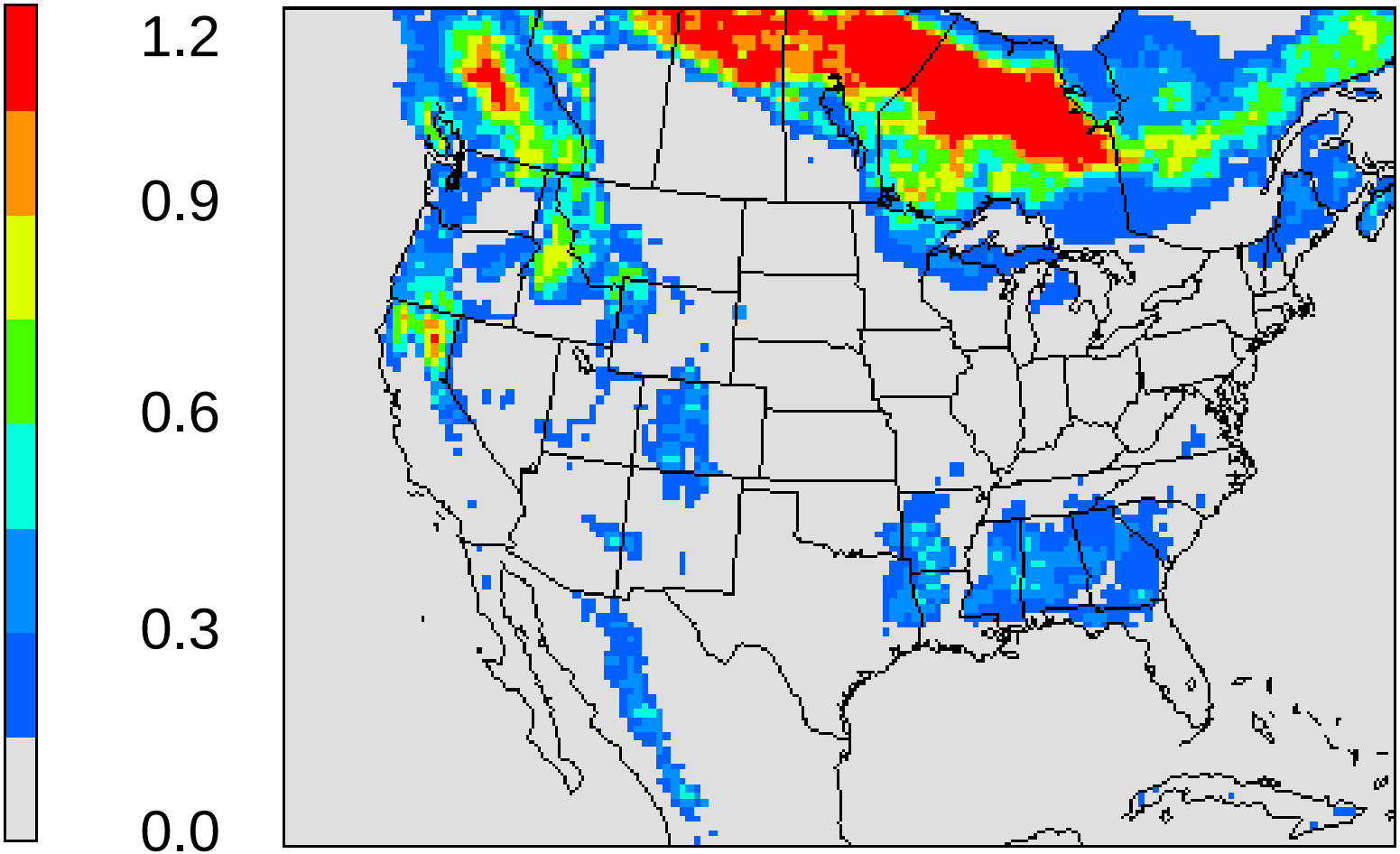
CMAQ - Seasonal Average SOA Simulations





Biogenic Secondary Aerosol

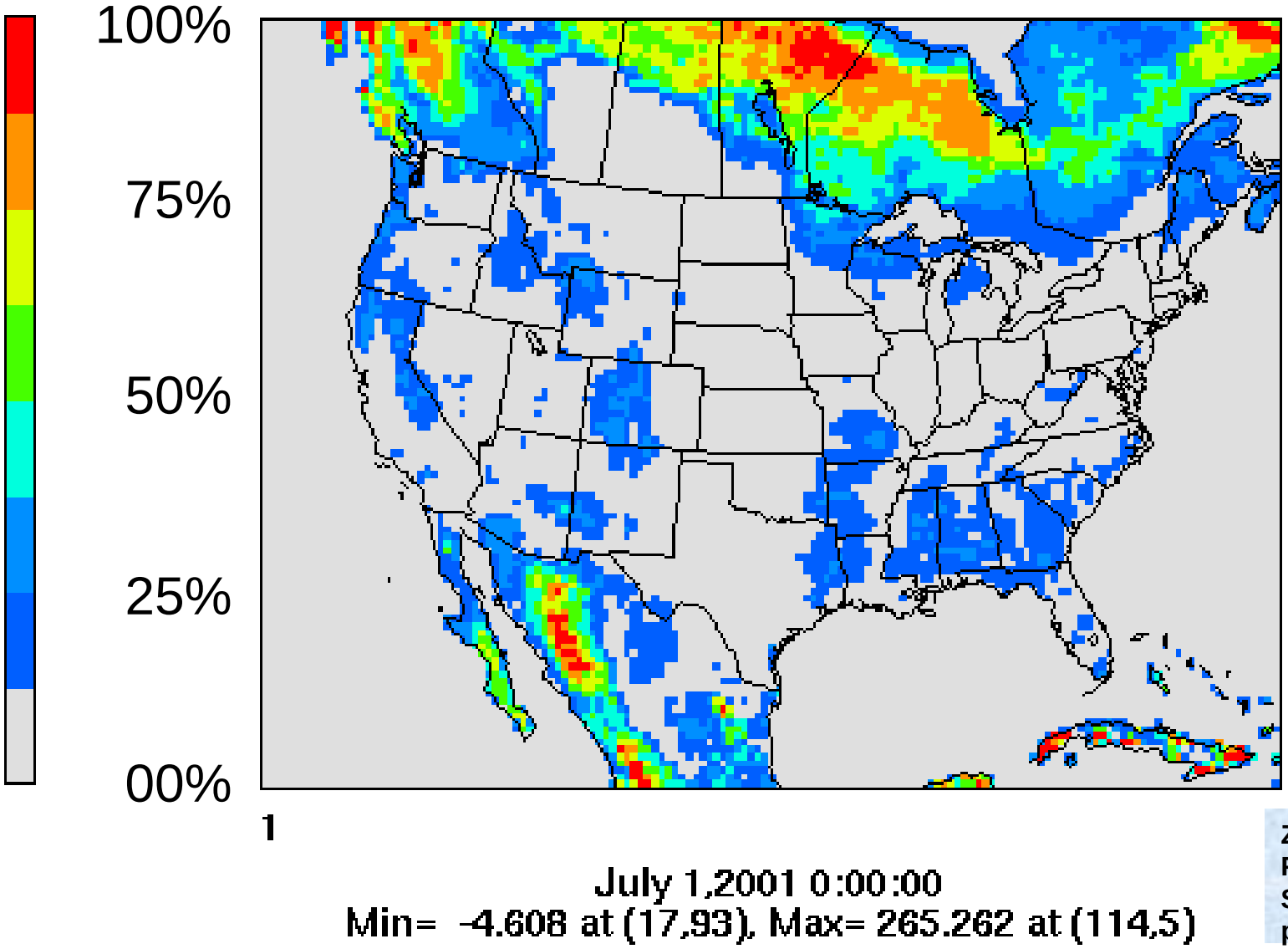
Difference of monthly mean between Canopy and Baseline runs



Zhang, Fuentes and Stockwell, in preparation

Biogenic Secondary Aerosol

Percent difference of monthly mean between Canopy and Baseline runs



Zhang, Fuentes and Stockwell, in preparation

This large production of organic aerosols due to the processing of biologically emitted organic compounds in forest canopies is sufficient to affect climate.

- **Solar radiation calculations are needed to assess if this effect represents heating or cooling.**
- **Best guess now is that it is cooling.**
- **In that case the aerosol mitigates the effects of greenhouse gases to some degree.**

Current Research Efforts

- RACM2 mechanism development and implementation in WRF and CMAQ
- Nighttime nitrate radical field studies
- Construction of a chemical reaction chamber
- Investigations of the neural toxic effects of mercury

Key Research Activities and Objectives to Improve the Atmospheric Chemistry in CMAQ and WRF/Chem

(1) Extend RACM2 to include organic aerosol formation.
(2) Implement the Regional Atmospheric Chemical Mechanism (RACM2) and associated new aerosol chemistry in models.
(3) Perform sensitivity tests to identify key parameters and reaction rates to prioritize chemical mechanism development efforts.
(4) Given key sensitivities refine the chemical mechanism.
(5) Compare simulations with satellite, aircraft and field data.

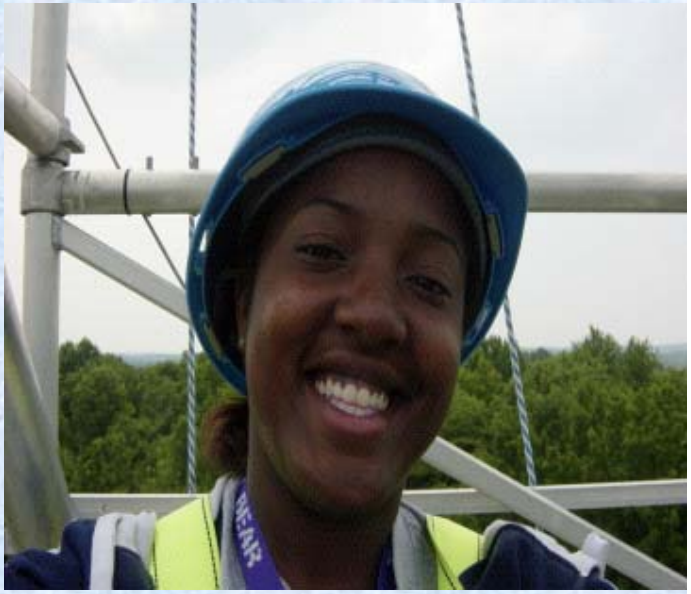
Conclusions

- **Large quantities of organic compounds are emitted from biological sources.**
-
- **A very large fraction of biologically emitted organic compounds are alkenes and their chemistry is complicated.**

- **Field studies at Beltsville, DRI and other sites are contributing to improved understanding of problems in chemical mechanisms.**

- **New modeling results suggest that the processing of biologically emitted organic compounds in forest canopies is unrecognized source of climate forcing that probably mitigates the effects of greenhouse gases to some degree.**

Some of the People Who Really Do the Work



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