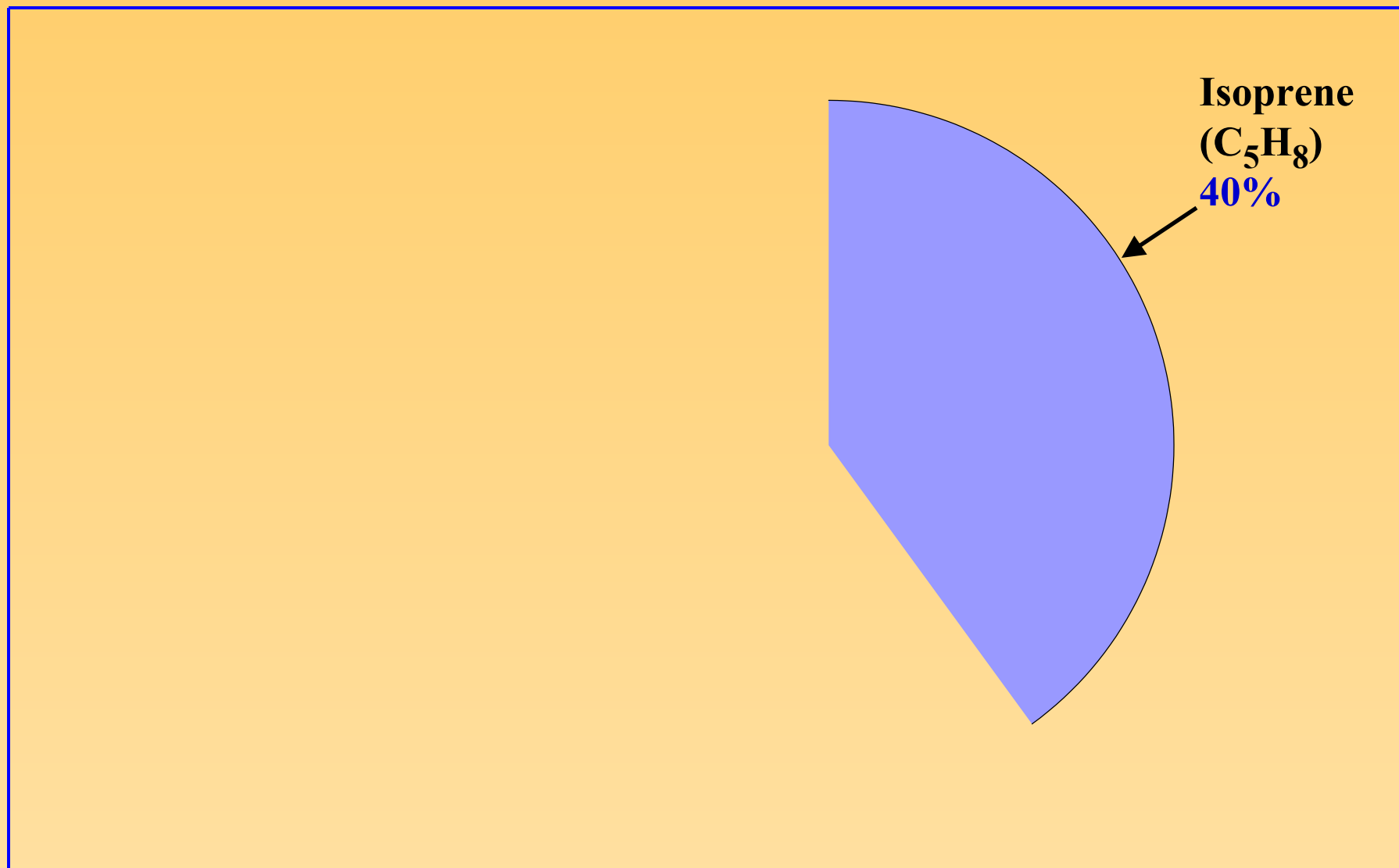


A large white blimp is being inflated on a grassy field. The blimp is long and cylindrical with a tail section. Several people are standing around the base of the blimp, and there are tables and equipment on the ground. The background shows a line of trees under a clear blue sky.

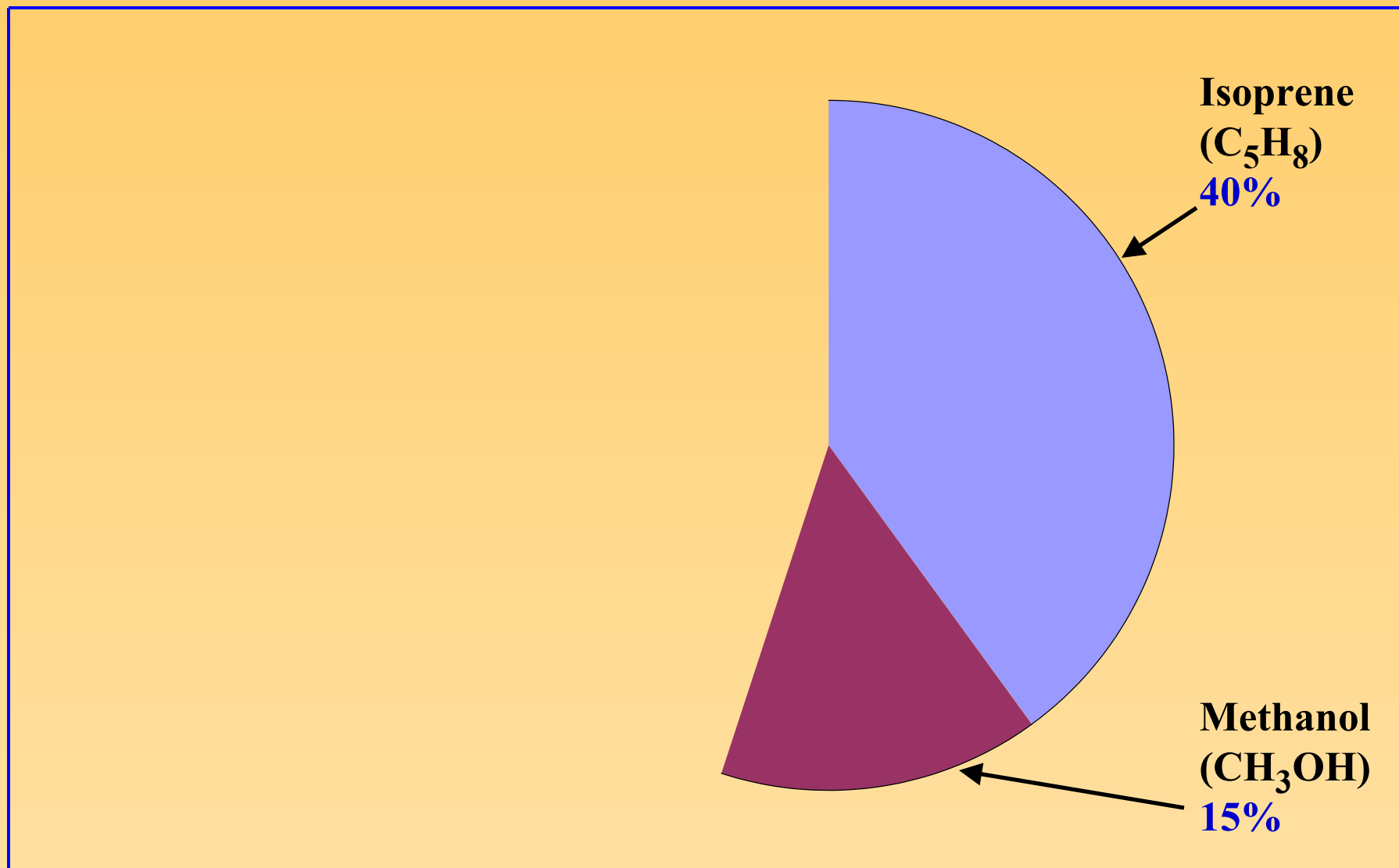
Leaf, Canopy, Landscape, and Regional Measurements for Developing and Evaluating Biogenic VOC Emission Models

**Alex Guenther, Jim Greenberg, Peter Harley, Thomas Karl,
Eiko Nemitz, Andrew Turnipseed, and Christine Wiedinmyer
Biosphere-Atmosphere Interactions Group
Atmospheric Chemistry Division
National Center for Atmospheric Research
Boulder Colorado, USA**

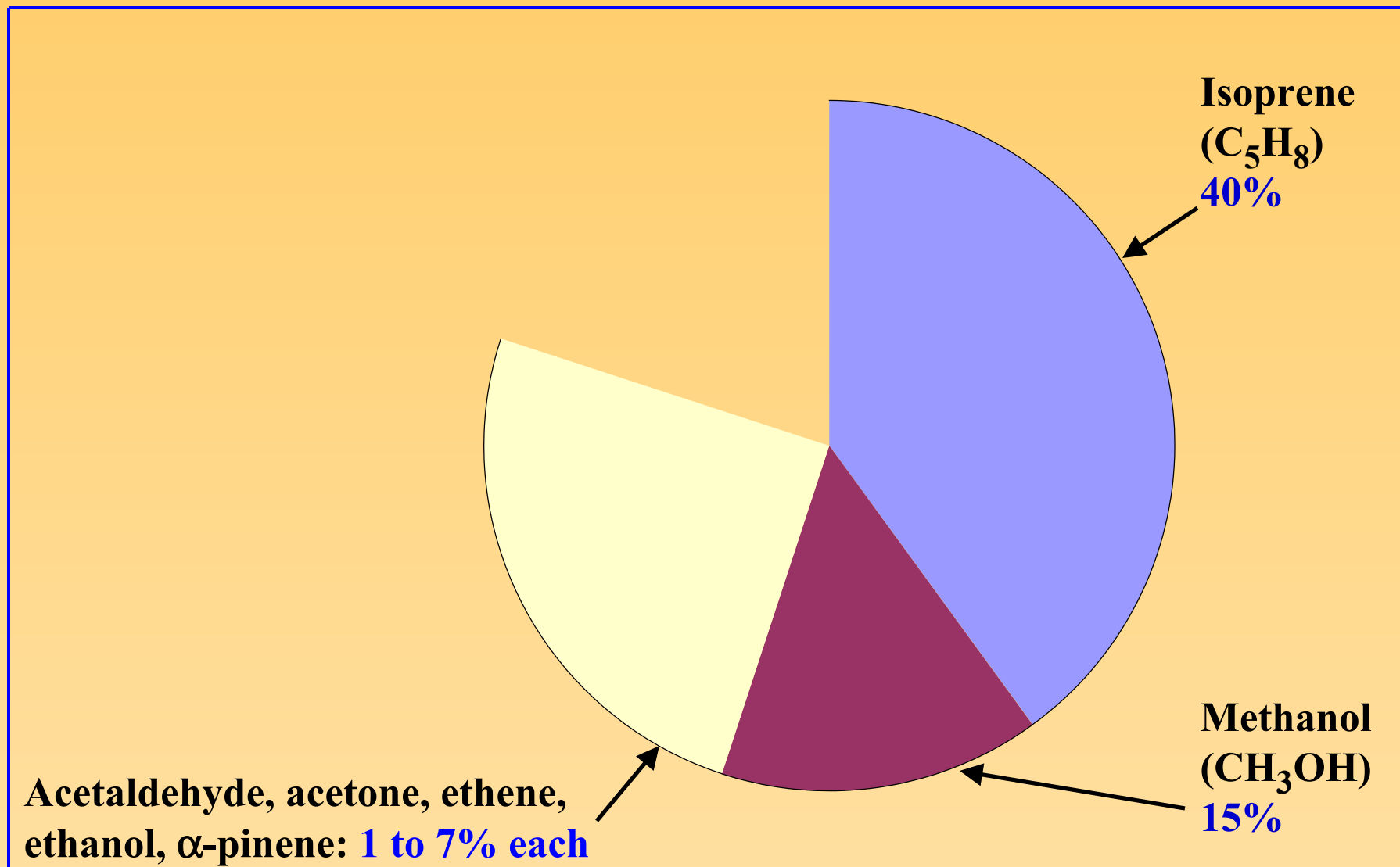
Biogenic Volatile Organic Compounds: Annual Global Total Emission > 1.5 Gt



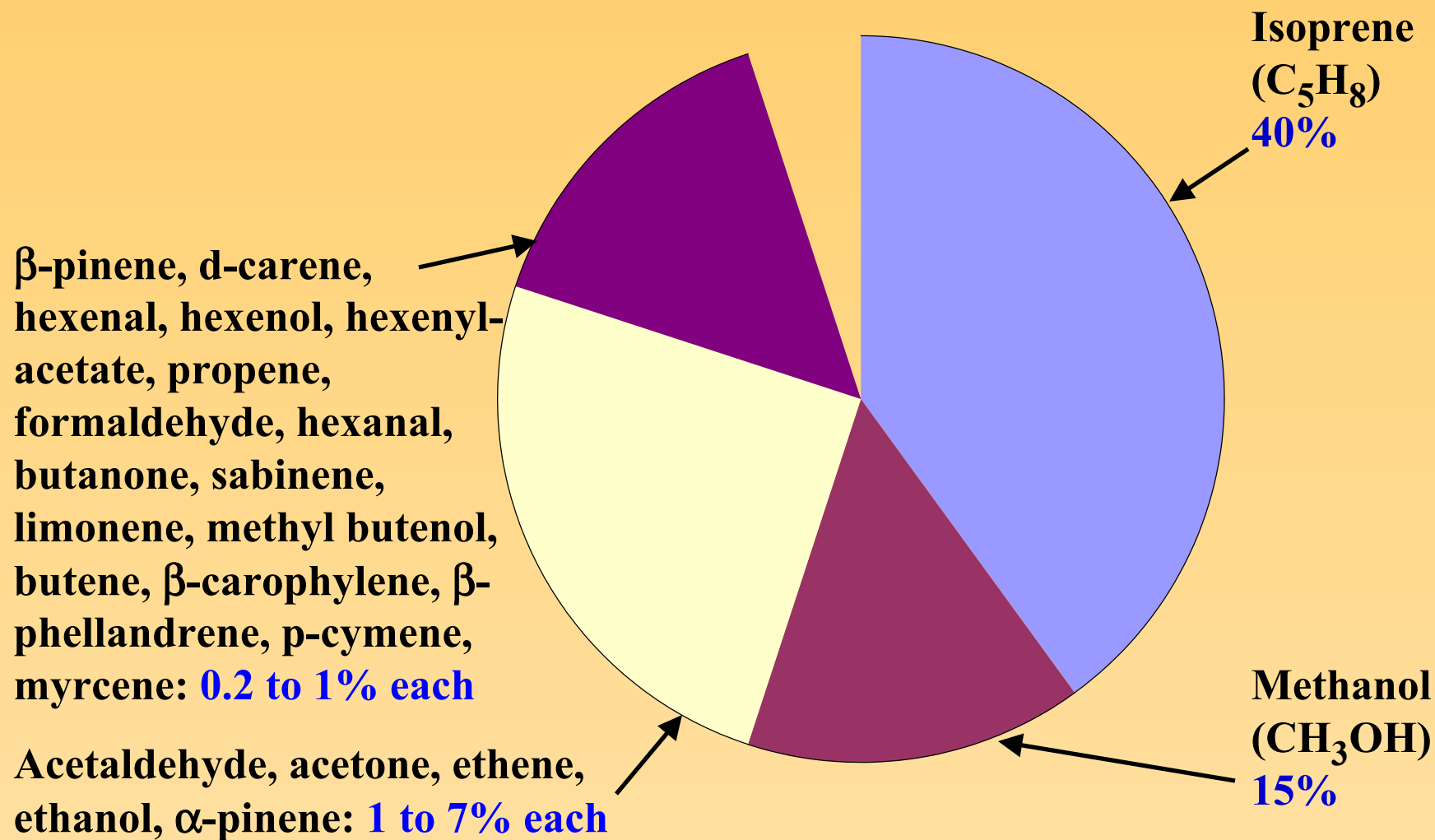
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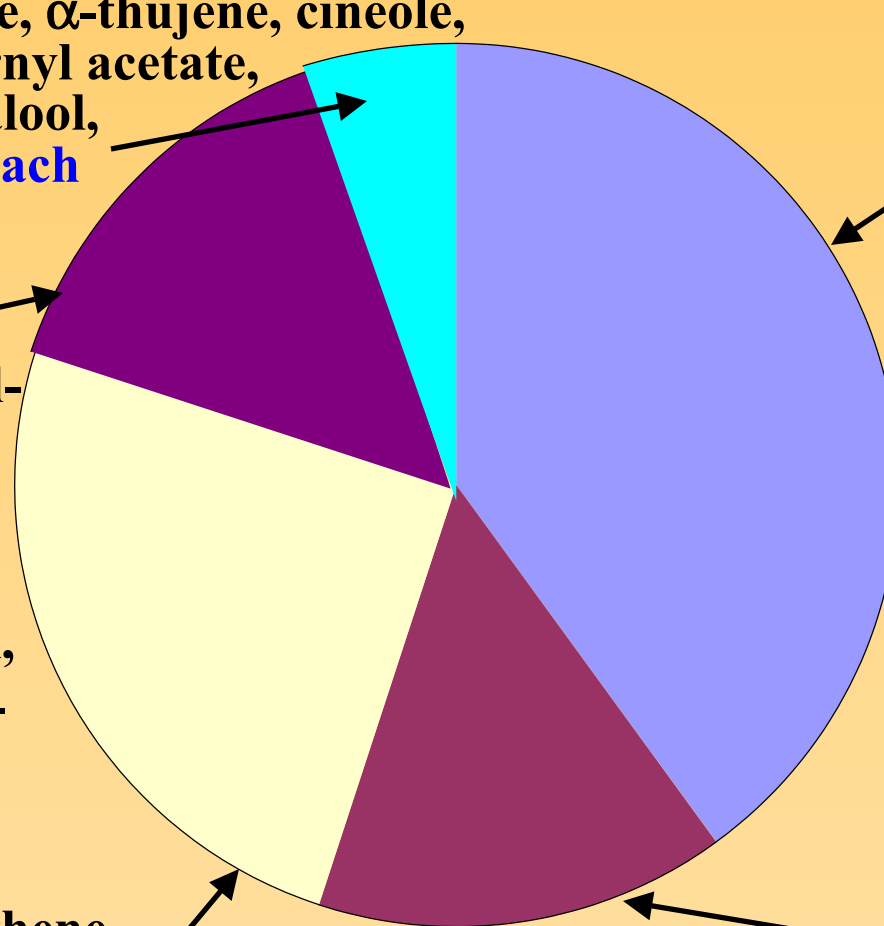


Biogenic Volatile Organic Compounds: Annual Global Total Emission > 1.5 Gt

Formic acid, acetic acid, ethane, toluene, camphene, terpinolene, α -terpinolene, α -thujene, cineole, ocimene, γ -terpinene, bornyl acetate, camphor, piperitone, linalool, tricyclene: **0.04 to 0.2% each**

β -pinene, d-carene, hexenal, hexenol, hexenyl-acetate, propene, formaldehyde, hexanal, butanone, sabinene, limonene, methyl butenol, butene, β -carophylene, β -phellandrene, p-cymene, myrcene: **0.2 to 1% each**

Acetaldehyde, acetone, ethene, ethanol, α -pinene: **1 to 7% each**



Isoprene
(C₅H₈)
40%

Methanol
(CH₃OH)
15%

Biogenic Volatile Organic Compounds: Annual Global Total Emission > 1.5 Gt

Formic acid, acetic acid, ethane, toluene, camphene, terpinolene, α -terpinolene, α -thujene, cineole, ocimene, γ -terpinene, bornyl acetate, camphor, piperitone, linalool, tricyclene: **0.04 to 0.2% each**

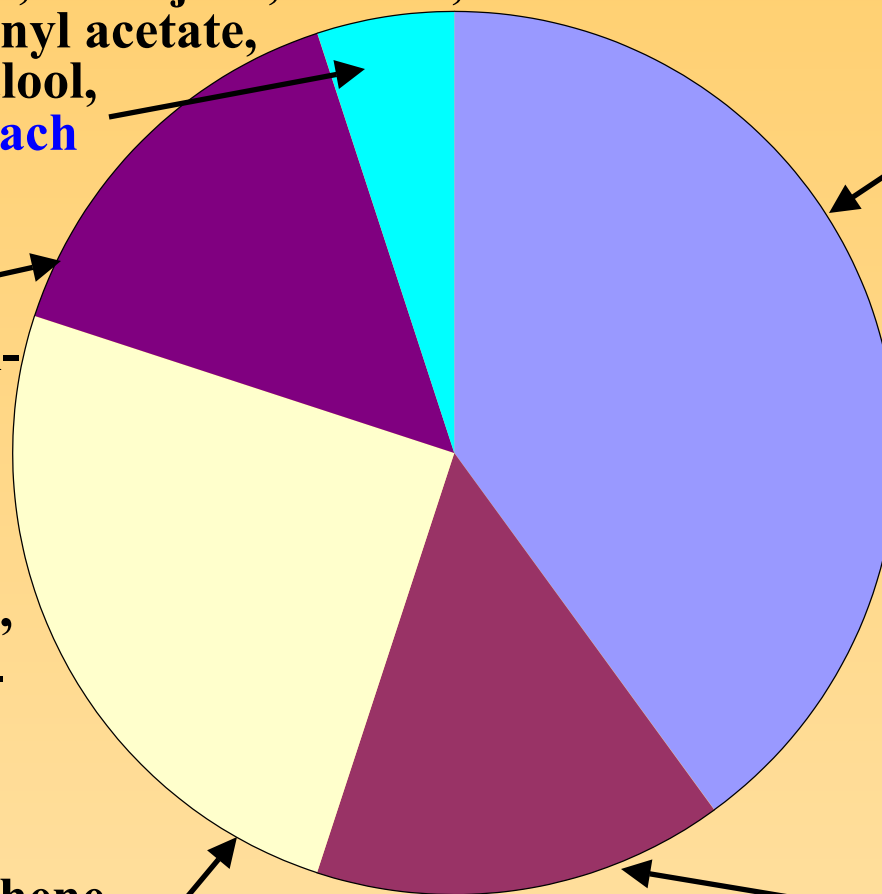
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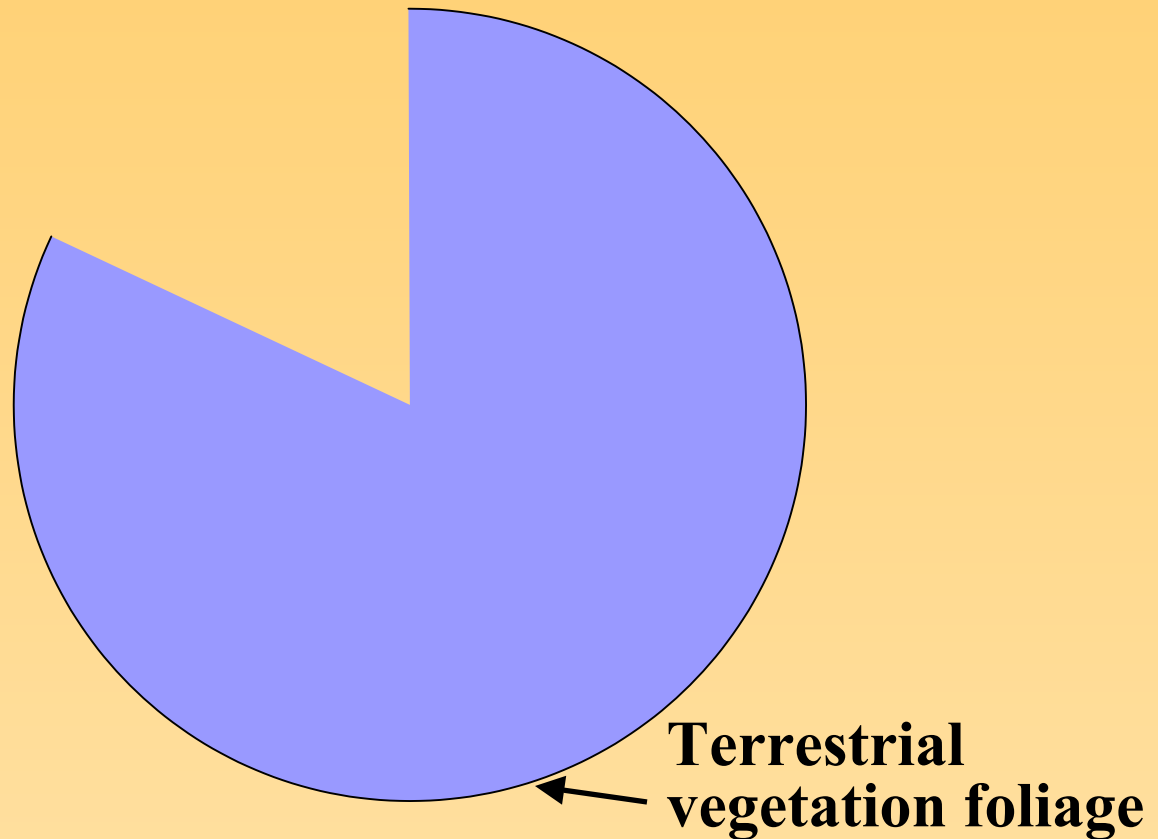
Isoprene
(C_5H_8)
40%

Various compounds may dominate annual emissions at specific locations

Methanol
(CH_3OH)
15%

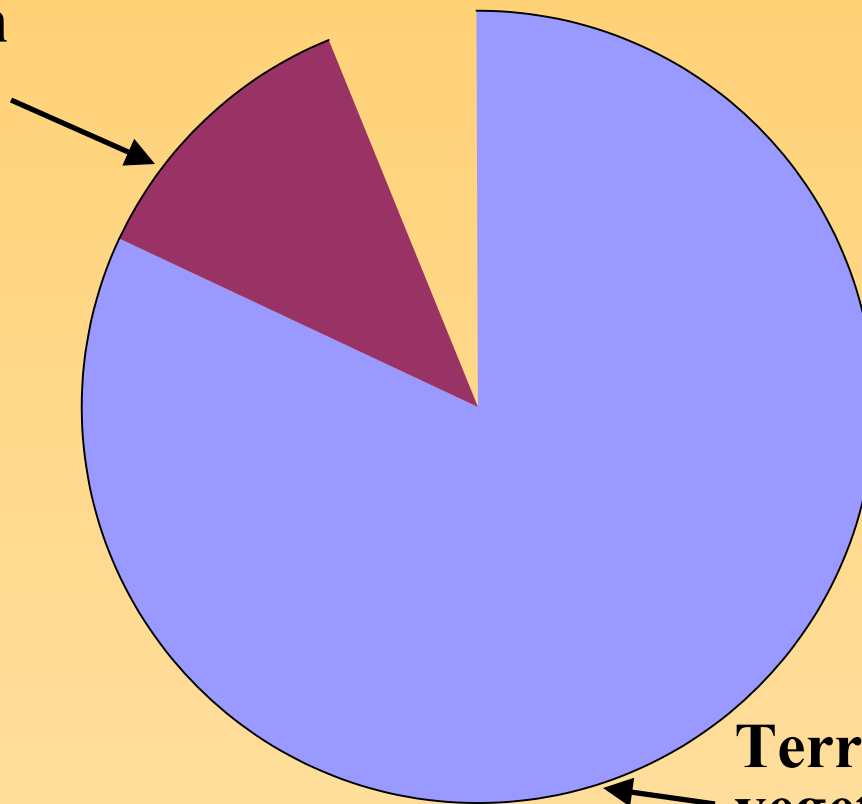


Biogenic Volatile Organic Compound Sources: Annual Global Total Emission > 1.5 Gt



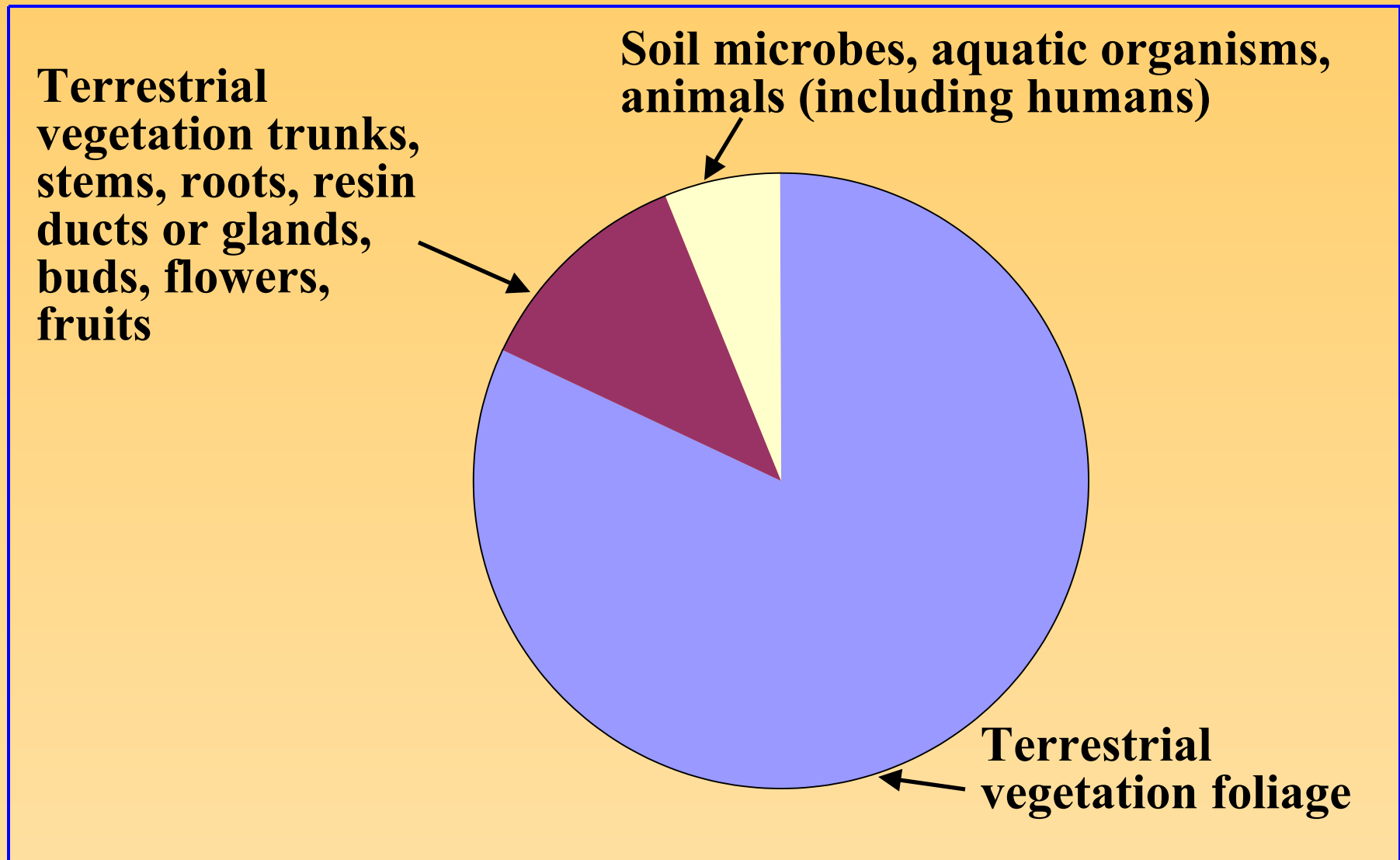
Biogenic Volatile Organic Compound Sources: Annual Global Total Emission > 1.5 Gt

**Terrestrial
vegetation trunks,
stems, roots, resin
ducts or glands,
buds, flowers,
fruits**



**Terrestrial
vegetation foliage**

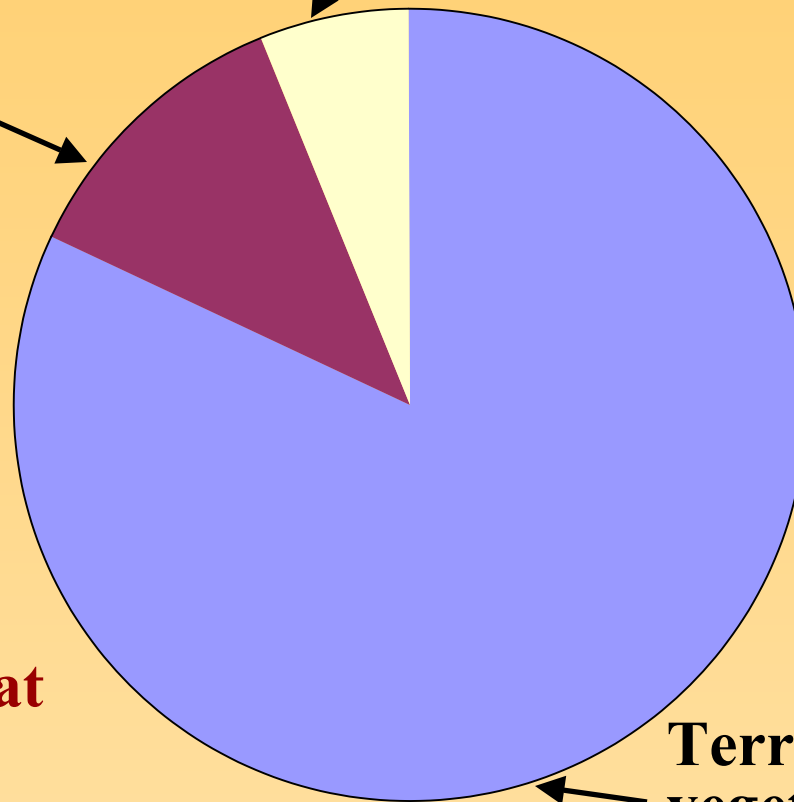
Biogenic Volatile Organic Compound Sources: Annual Global Total Emission > 1.5 Gt



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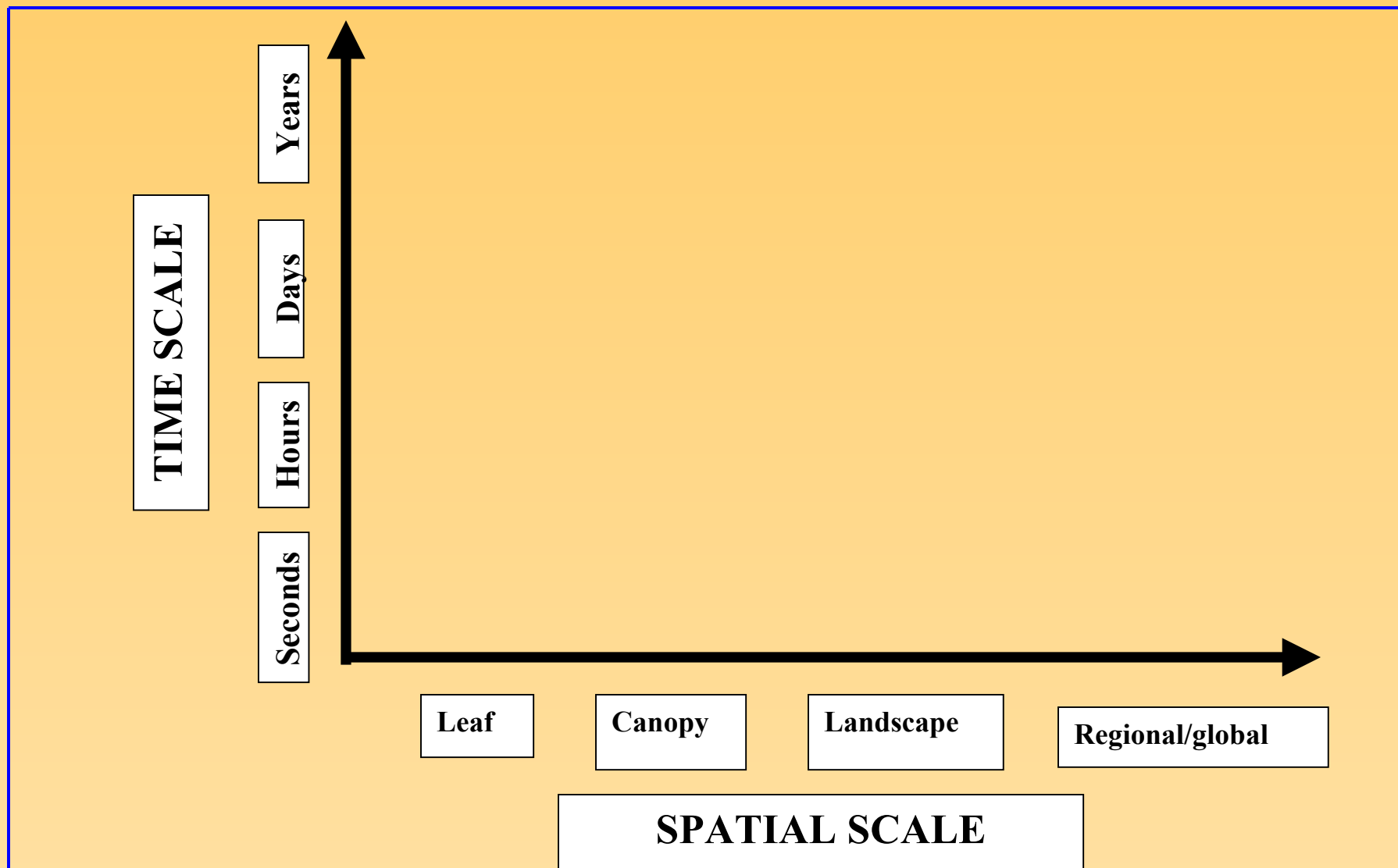
Soil microbes, aquatic organisms,
animals (including humans)



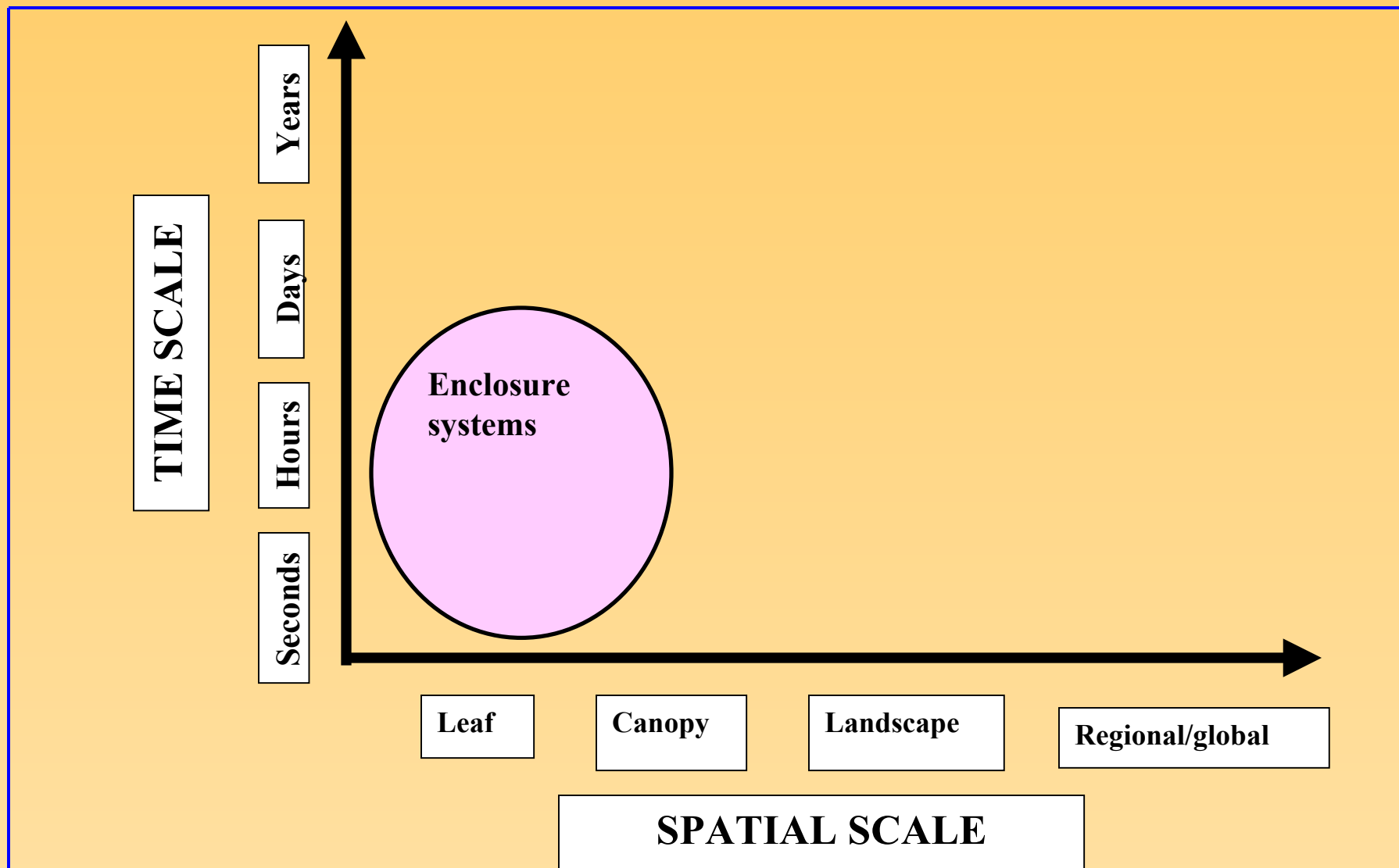
Many of these
sources can make a
major contribution at
a specific location
and time

Terrestrial
vegetation foliage

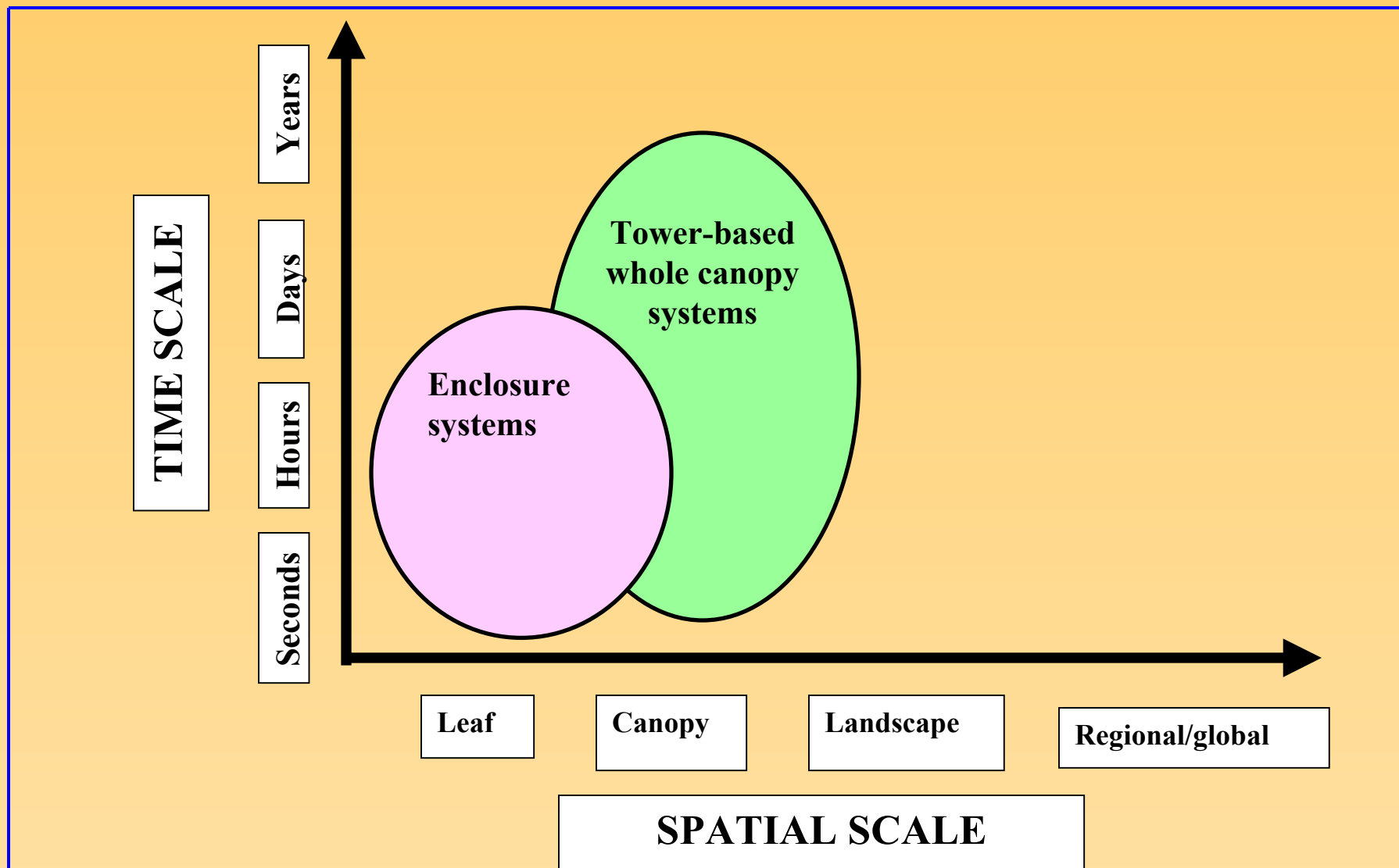
Tools for Investigating Trace Gas Fluxes



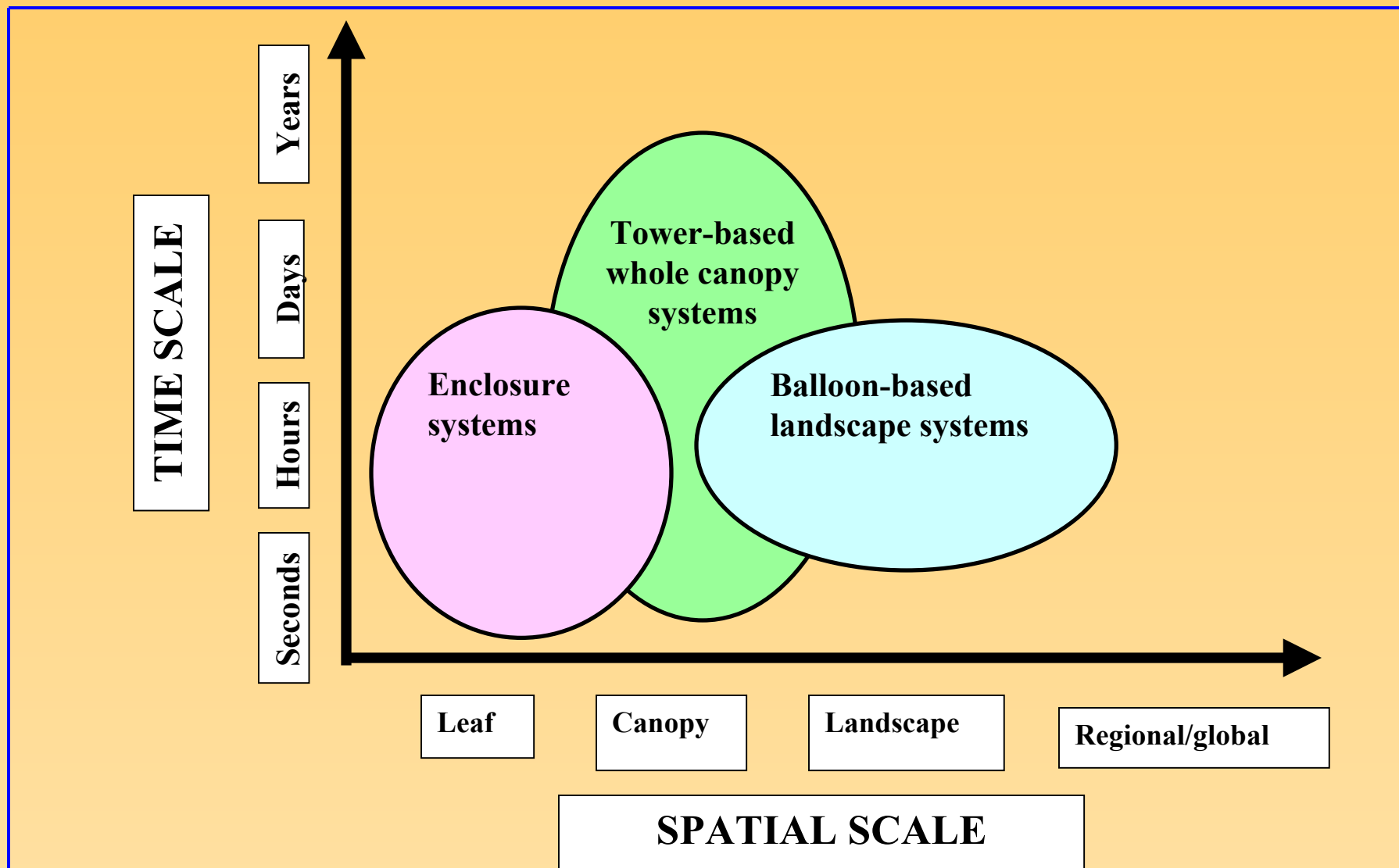
Tools for Investigating Trace Gas Fluxes



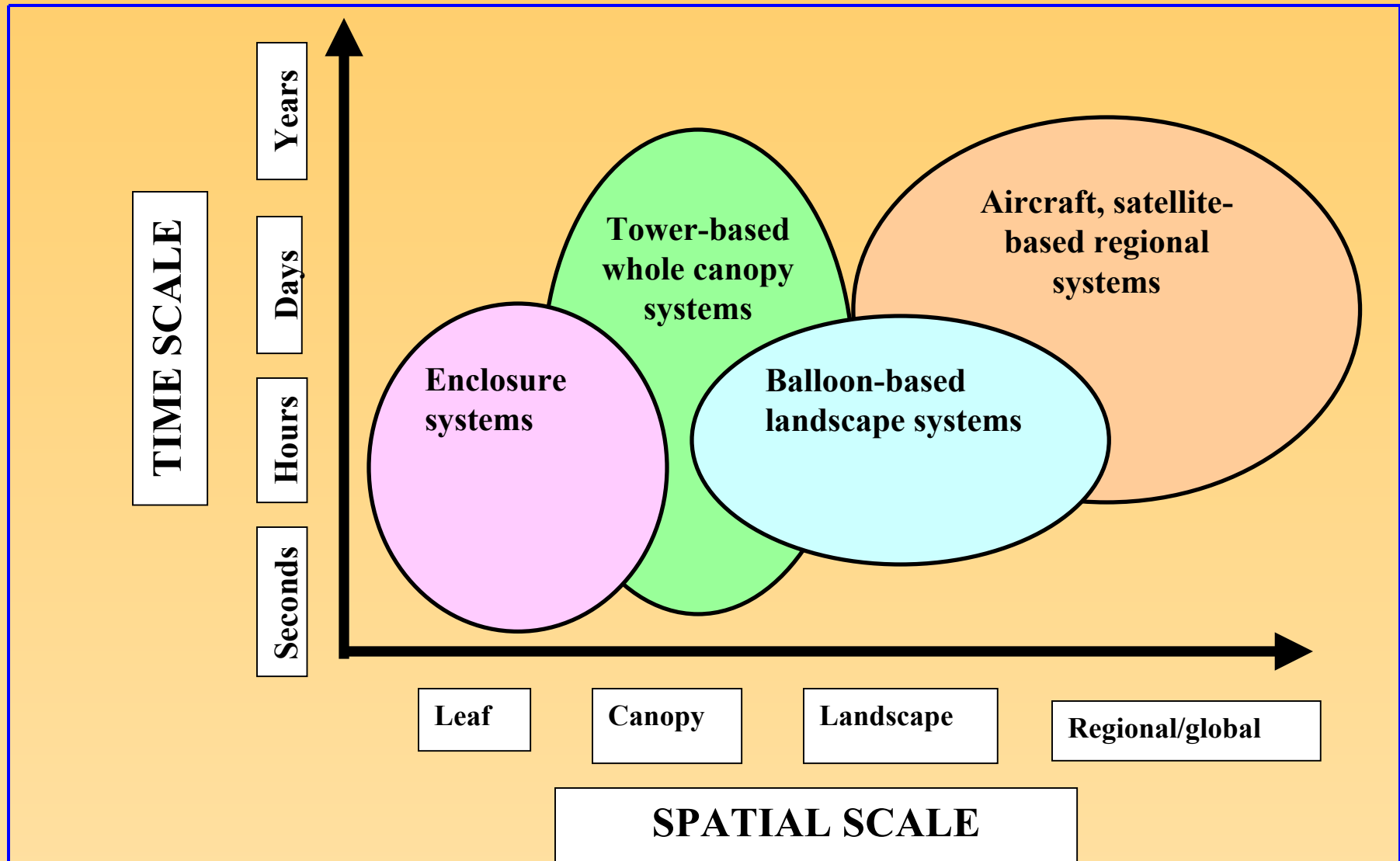
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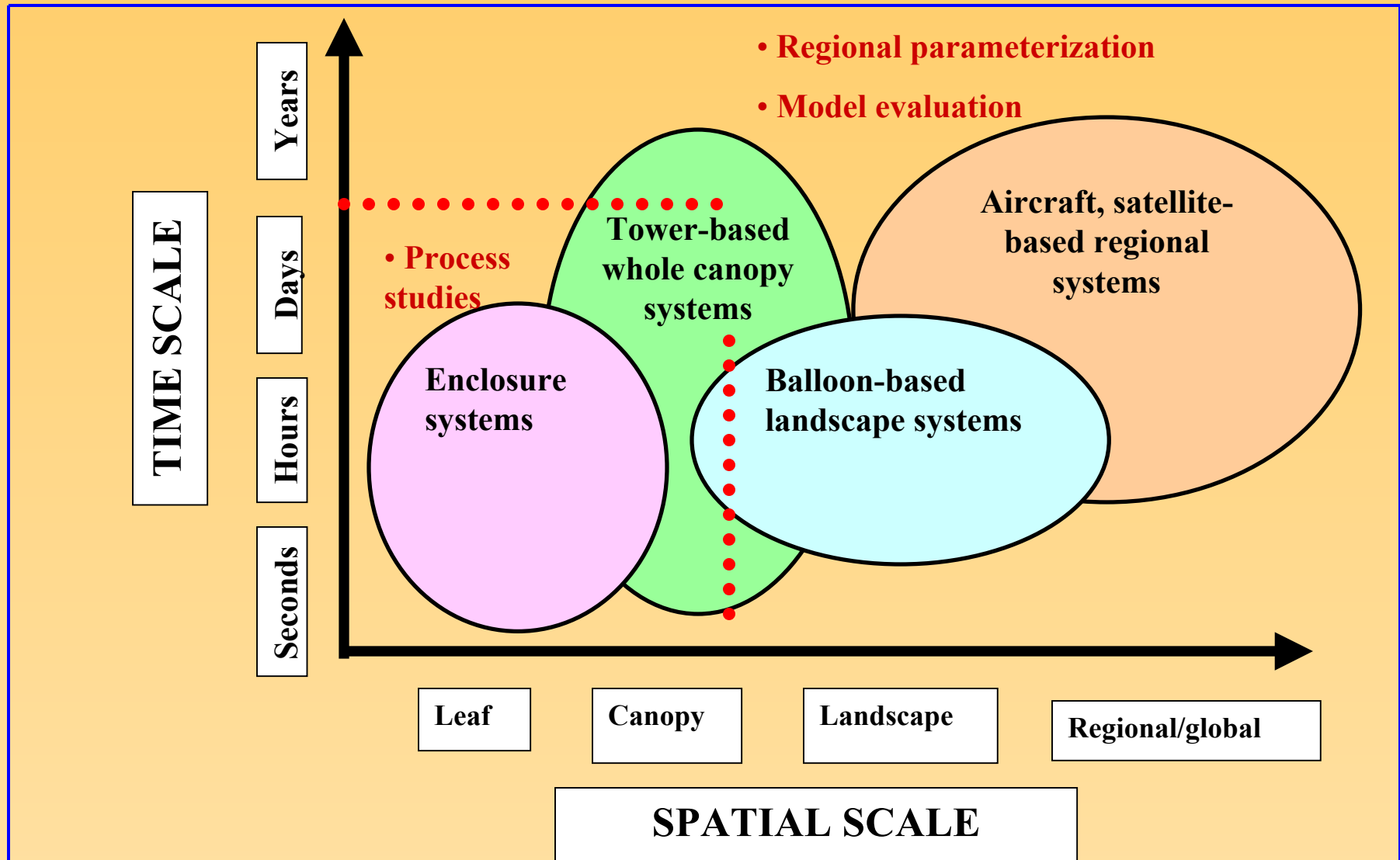
Tools for Investigating Trace Gas Fluxes



Tools for Investigating Trace Gas Fluxes



Tools for Investigating Trace Gas Fluxes



Component-scale: Enclosure measurements



Flux Methods

- Leaf, branch, whole plant enclosures
- With or without environmental controls
- In-situ analysis or store and transport samples

Applications

- Combine emission factors with vegetation surveys to predict landscape scale emissions
- Develop algorithms to simulate variations due to environmental conditions
- Compounds that are so reactive that they do not escape the canopy

Combining Emission Factors with Vegetation Surveys

<u>California Oaks</u>	<u>BEIS: Lamb et al. 1987</u>	<u>BEIS2: Guenther et al. 1994</u>
Quercus agrifolia	23	70
Q. berberidifolia	23	70
Q. chrysolepis	23	70
Q. douglasii	23	70
Q. engelmannii	23	70
Q. lobata	23	70
Q. kelloggii	23	70
Q. wislizenii	23	70

**Isoprene emission factor ($\mu\text{g g}^{-1} \text{h}^{-1}$)
at leaf temperature of 30°C and PAR
of 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$**

**Oak trees contribute
more than 70% of
the total isoprene
emissions**

Combining Emission Factors with Vegetation Surveys

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Quercus agrifolia	23	70	31.1
Q. berberidifolia	23	70	---
Q. chrysolepis	23	70	21.9
Q. douglasii	23	70	7.7
Q. engelmannii	23	70	21.9
Q. lobata	23	70	3.0
Q. kelloggii	23	70	21.9
Q. wislizenii	23	70	11.0

**Are isoprene
emissions from
California oaks
lower than other
oaks ?**

**Isoprene emission factor ($\mu\text{g g}^{-1} \text{h}^{-1}$)
at leaf temperature of 30°C and PAR
of $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$**

**Oak trees contribute
more than 70% of
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emissions**

Isoprene emissions from California oaks are similar to other N. American oaks

<u>California Oaks</u>	<u>BEIS: Lamb et al. 1987</u>	<u>BEIS2: Guenther et al. 1994</u>	<u>Benjamin et al. 1996</u>	<u>Geron et al. 2001</u>
Quercus agrifolia	23	70	31.1	77
Q. berberidifolia	23	70	---	73
Q. chrysolepis	23	70	21.9	48
Q. douglasii	23	70	7.7	71
Q. engelmannii	23	70	21.9	39
Q. lobata	23	70	3.0	86
Q. kelloggii	23	70	21.9	78
Q. wislizenii	23	70	11.0	74
Average	23	70	17	68

Isoprene emission factor ($\mu\text{g g}^{-1} \text{h}^{-1}$)
at leaf temperature of 30°C and PAR
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Why have the isoprene emission factors for N. American oaks changed ?

- **There may have been experimental errors.**
- **Most of the isoprene “emission factors” reported for various plant species in the literature do not account for differences in physiological activity.**
- **There may be differences in the isoprene emission rates of North American oaks.**

Why have the isoprene emission factors for N. American oaks changed ?

- There may have been experimental errors. **It is difficult to determine but there have been improvements in techniques: in-situ analysis, environmental controls, upper canopy observations.**
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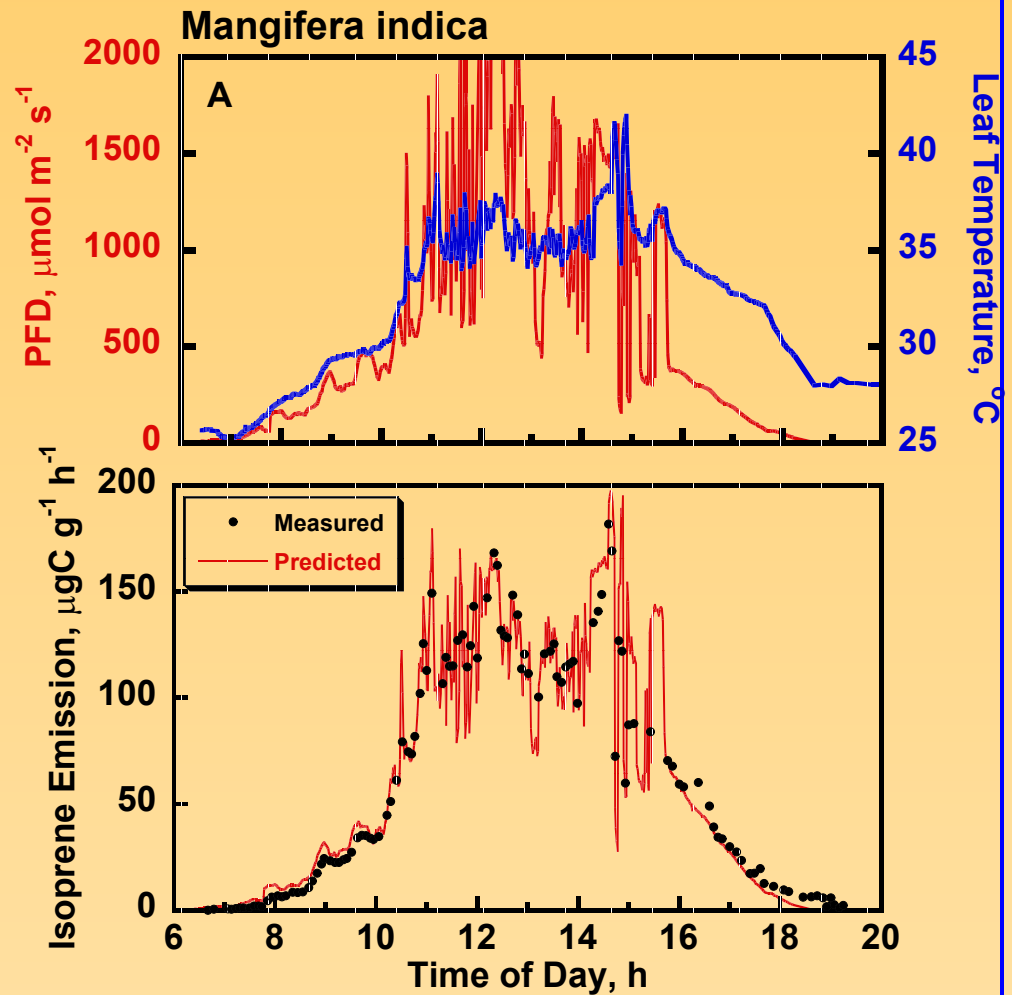
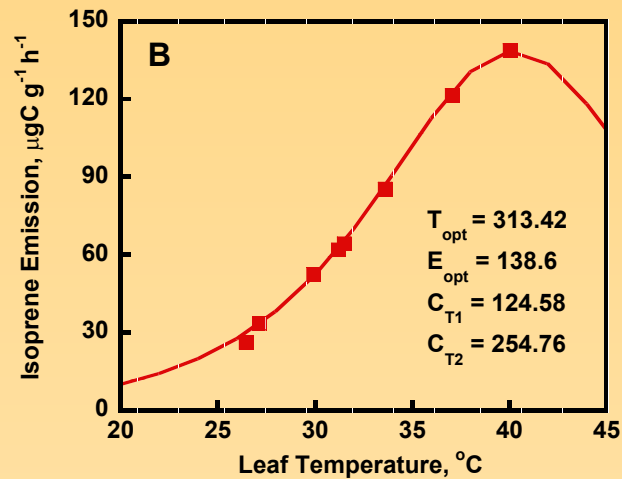
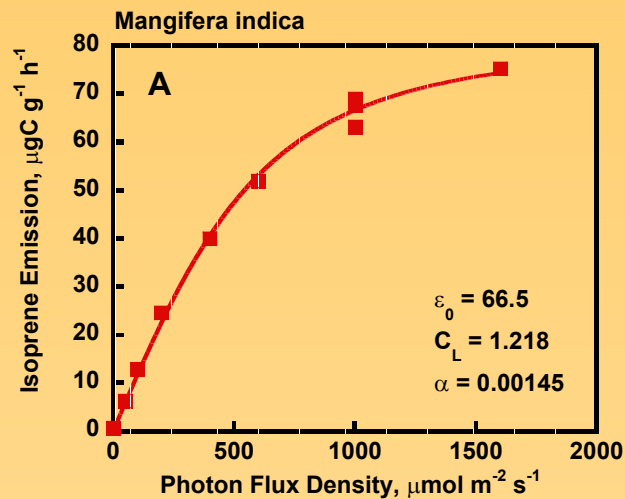
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- There may be differences in the isoprene emission rates of North American oaks. **The differences are minor relative to the physiological variability which remains only partly characterized.**

Leaf-scale observations: Develop algorithms to describe variations associated with environmental conditions

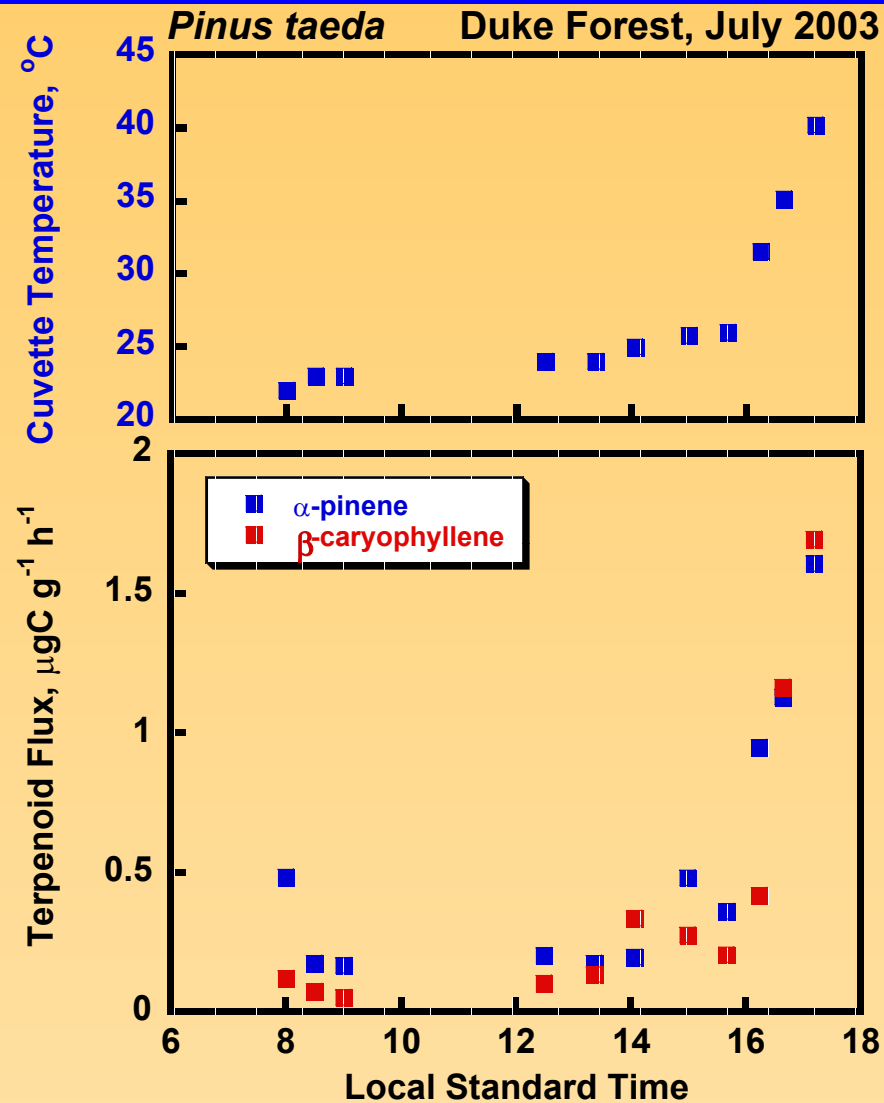
Current enclosure systems allow us to vary one parameter and keep others constant



Leaf-scale observations: Investigate compounds that are so reactive that they do not escape the canopy: Sesquiterpenes

Improved enclosures and analytical techniques allow us to look at more compounds.

Sesquiterpenes such as β -caryophyllene may contribute more to secondary organic aerosol production than monoterpenes for most landscapes



Canopy-scale: Tower measurements



Whole canopy isoprene fluxes measured by eddy covariance above Tapajos rainforest near Santarem, Brazil (Amazonia)

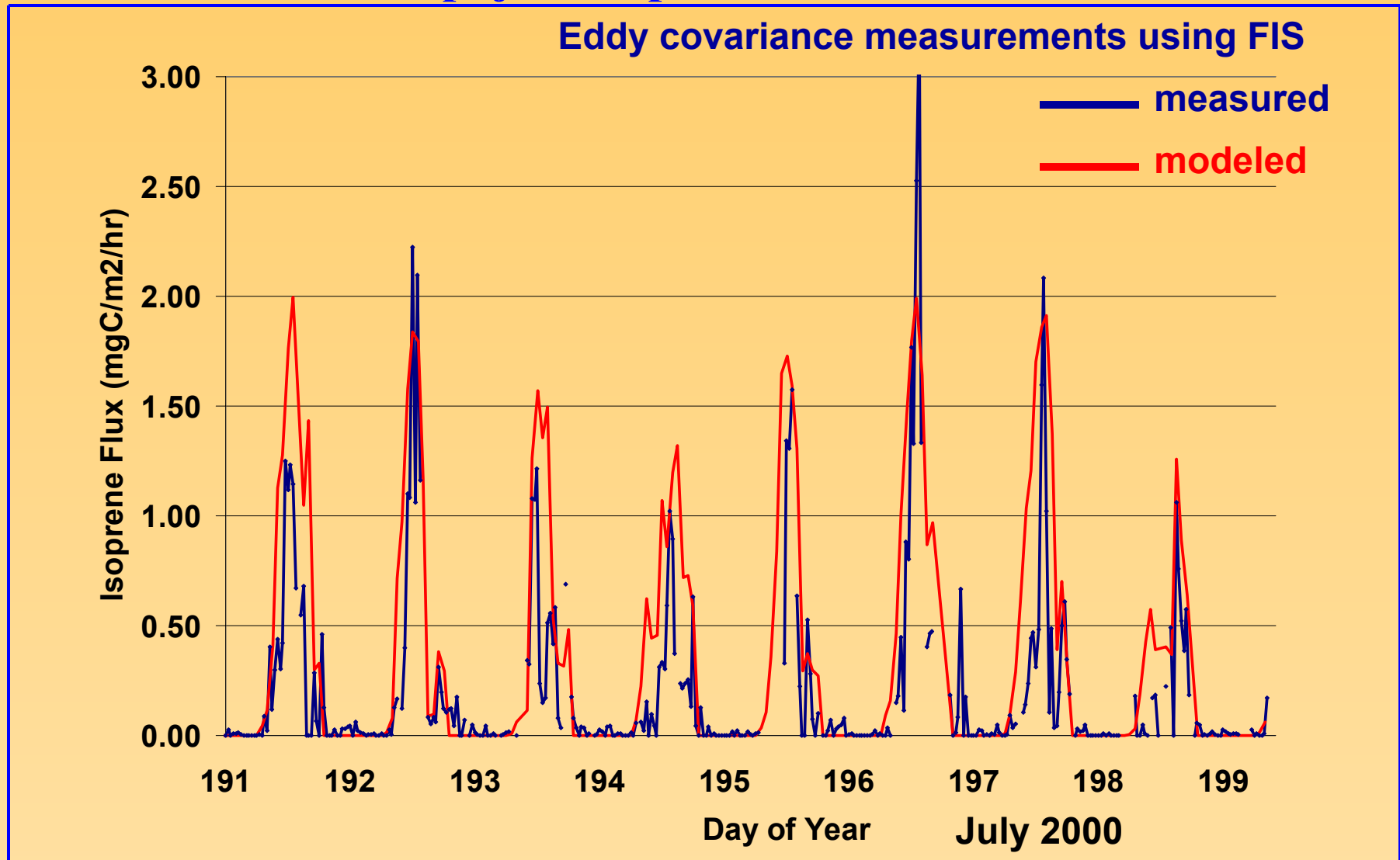
Flux Methods

- Eddy Covariance
- Disjunct Eddy covariance
- Disjunct Eddy Accumulation
- Relaxed Eddy Accumulation
- Vertical Gradients

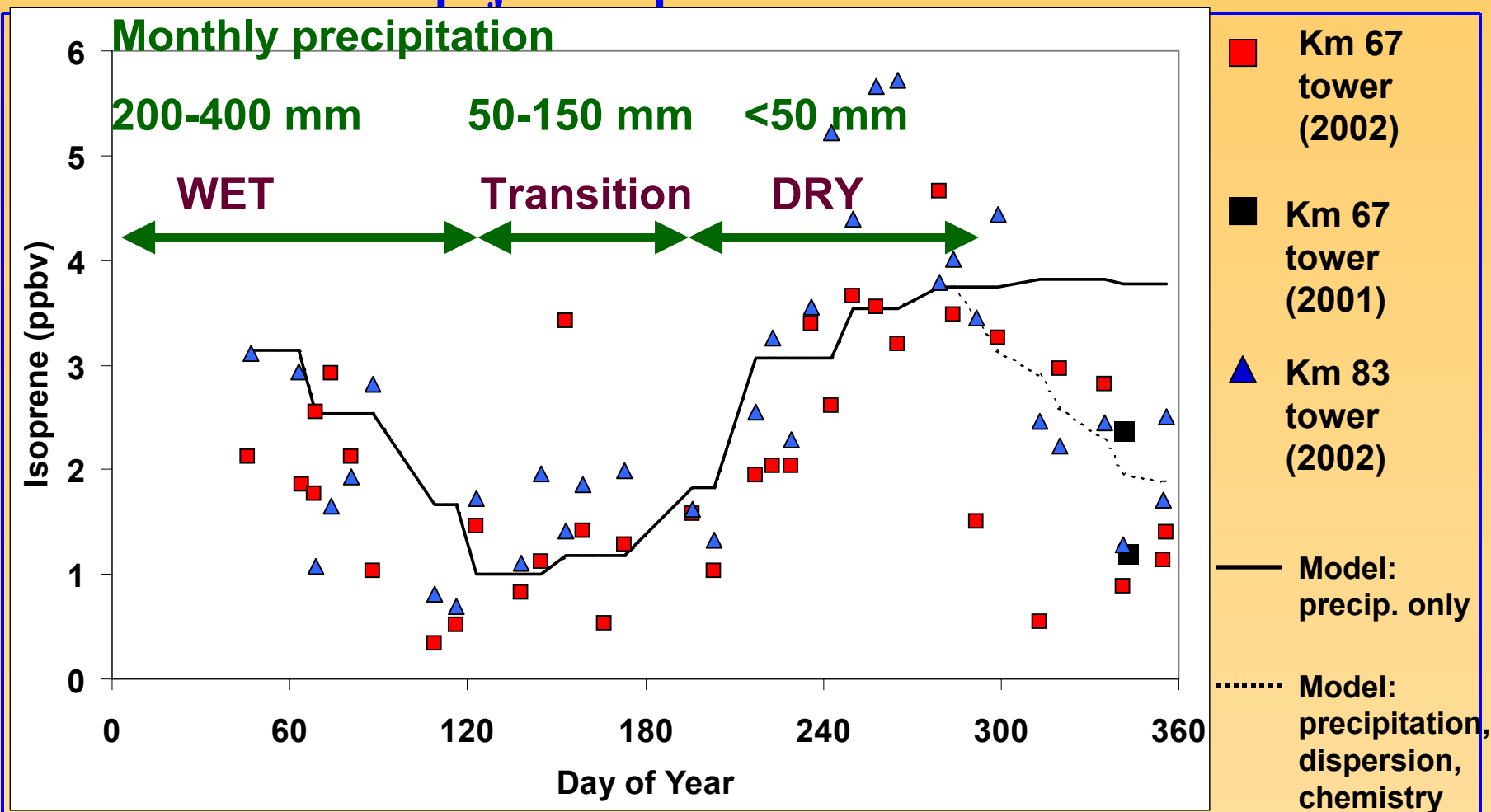
Applications

- Net ecosystem fluxes (emission and deposition)
- Investigate different ecosystem components with vertical gradients
- Diurnal variations
- Seasonal variations

Evaluating Diurnal Variations in Isoprene Fluxes from Tapajos Tropical Forest in Amazonia

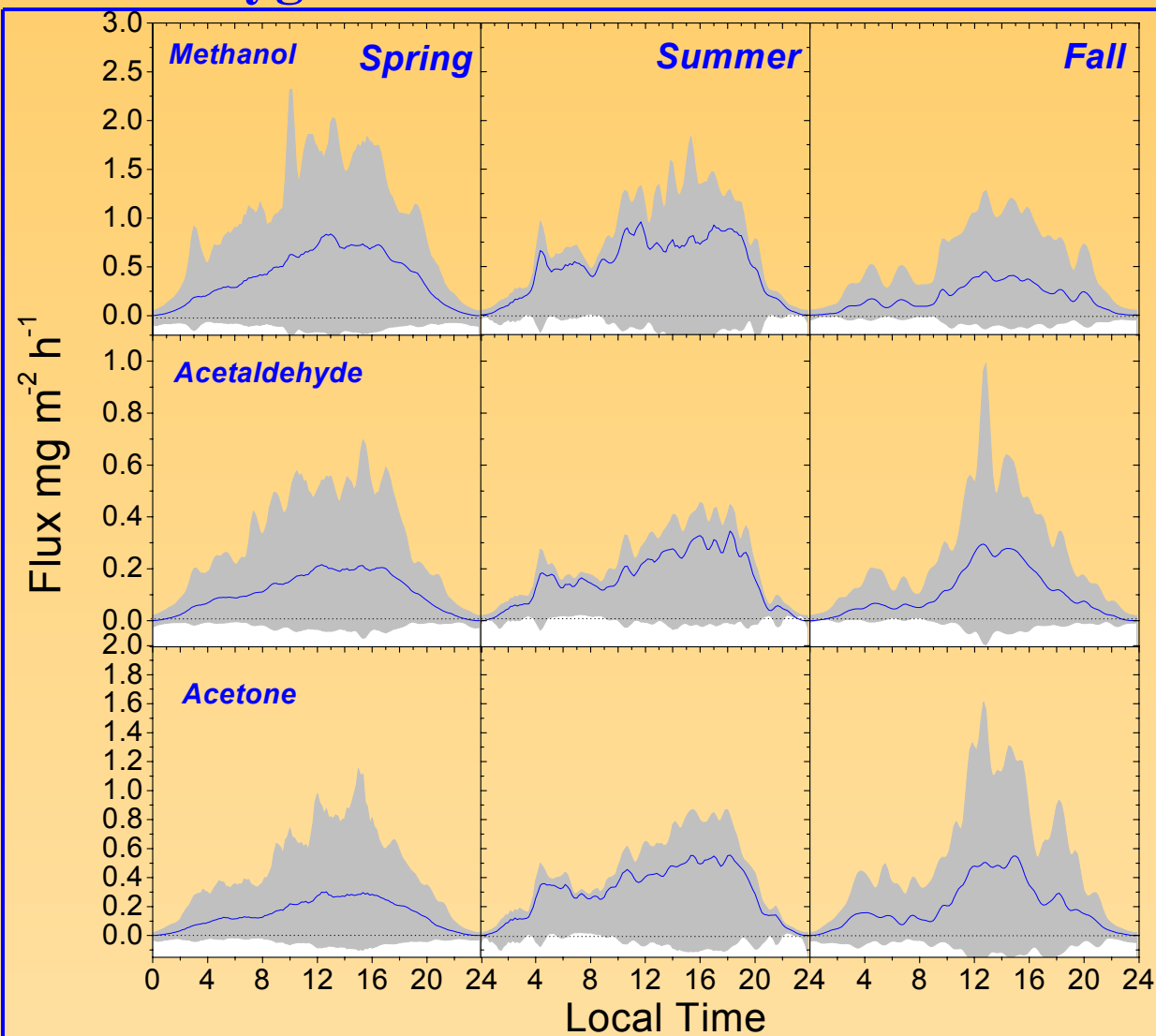


Characterizing Seasonal Variations in Isoprene at Tapajos Tropical Forest in Amazonia



Trostdorf, C., L. Gatti, A. Yamazaki, W. Martins, M. Potosnak, A. Guenther, Volatile Organic Compounds: Continuous measurements and isoprene fluxes in the Amazonian rainforest, submitted to *Atmos. Chem. Physics*

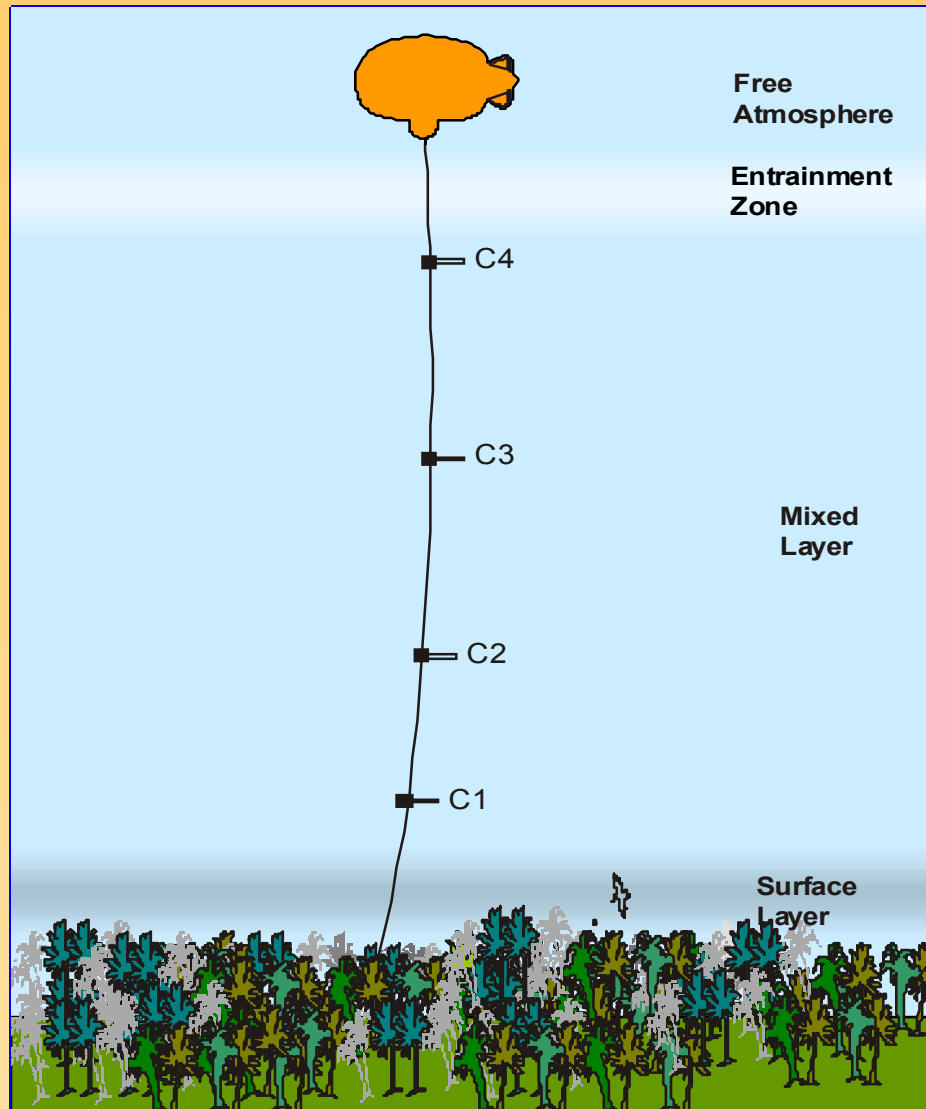
Characterizing Diurnal and Seasonal Variations in Oxygenated VOC Emissions from a Michigan Forest



Disjunct eddy covariance measurements using PTR-MS

Karl, T., A. Guenther, C. Spirig, A. Hansel and R. Fall, Seasonal variation of biogenic VOC emissions above a mixed hardwood forest in northern Michigan, *Geophys. Res. Letters*, in review.

Landscape-scale: Tethered Balloon Observations



Flux Methods

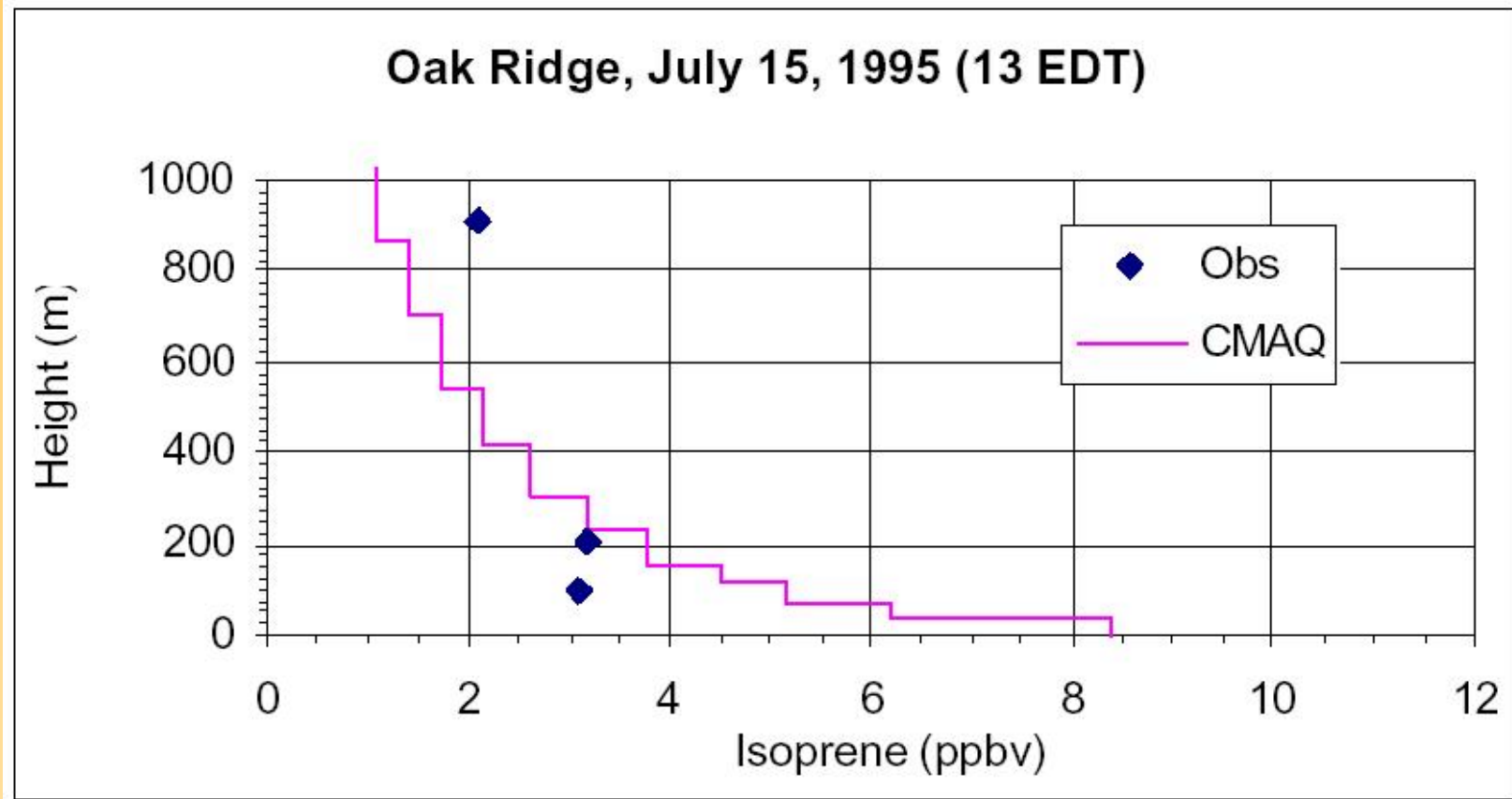
- Mass Balance
- Mixed Layer Gradient

Applications

- Integrate over areas of tens to hundreds of km²
- Better indicator of emissions than surface concentrations
- Can distinguish surface sources from entrainment above the boundary layer

Vertical Profiles of Concentrations are a Better Indicator of Emissions than just Surface Concentrations

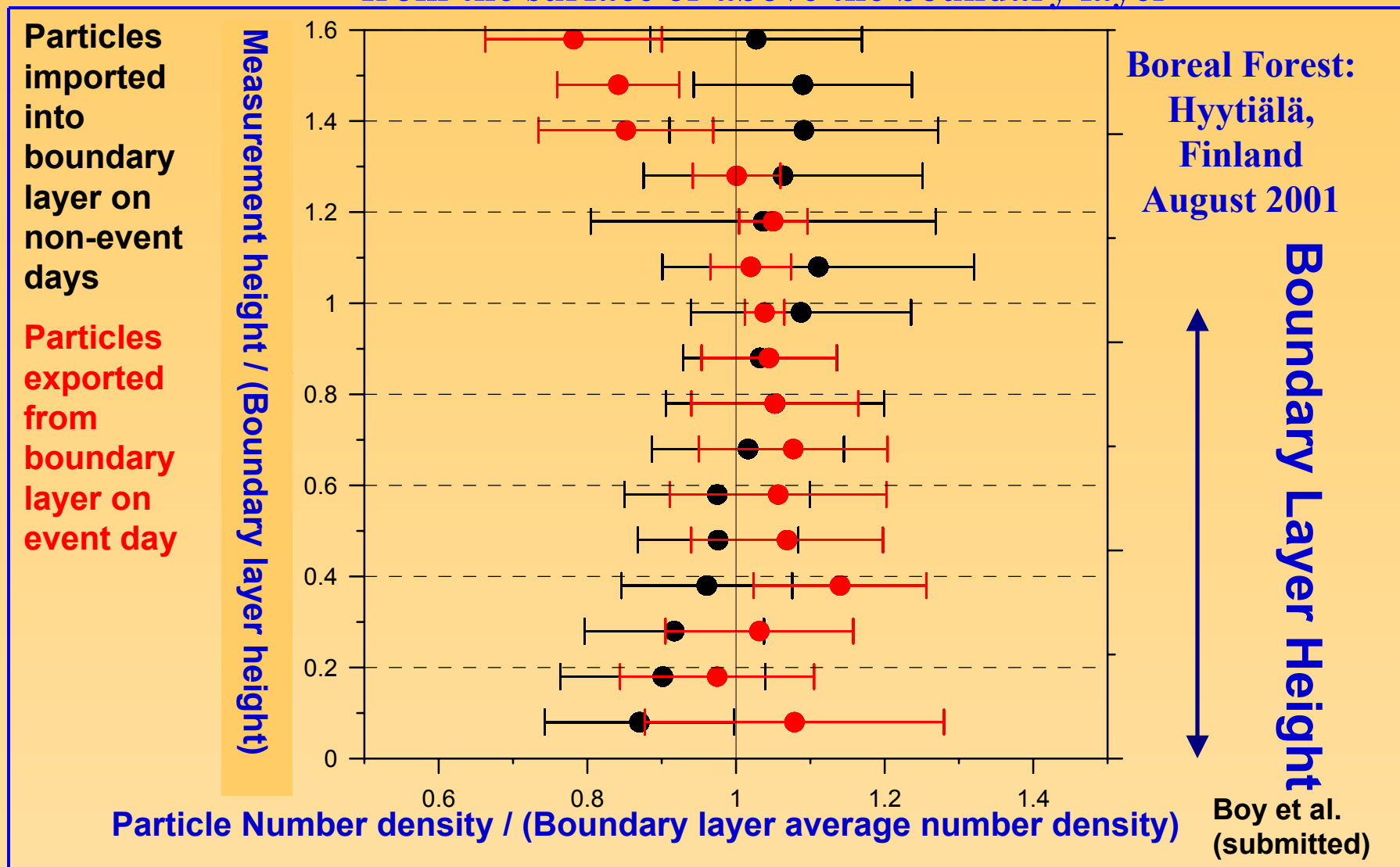
Tethered Balloon Vertical Profiles



Vertical transport was underestimated in model

- OPC (300-500nm), non-event days
- OPC (300-500nm), Aug 3

Vertical profiling can be used to determine whether the source is from the surface or above the boundary layer



Regional Scale: Aircraft Observations



1996: REA flux measurements of isoprene emissions from Central Africa using French ARAT aircraft (Guenther et al. 1999, Greenberg et al. 1999)

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1. Moderate size aircraft without vertical winds.

We will deploy a PTR-MS on a Brazilian Bandierante in 2004 and characterize biomass burning and biogenic VOC emissions from Amazonia using variance and mass balance methods.

We are considering similar efforts in South Africa and China

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Will deploy fast response sensors for VOC, O₃, NO_y, CO and other gases and use eddy covariance to characterize biogenic emissions, deposition and other fluxes from U.S. landscapes. But this will not be routine.



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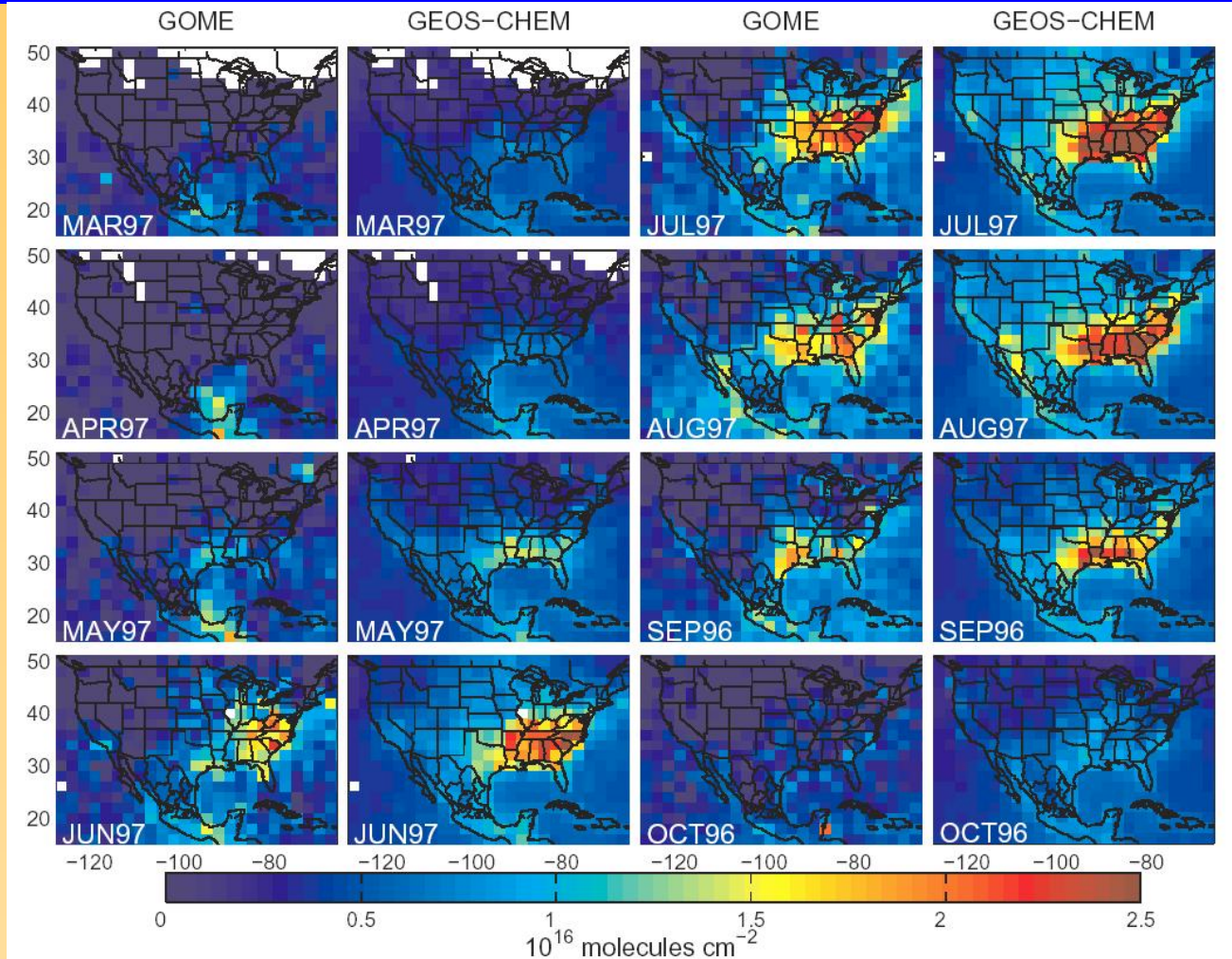


3. Low-cost aircraft with disjunct eddy accumulation flux system being developed by Purdue, NCAR and WSU and funded by NSF.

We plan to measure isoprene fluxes from U.S. forests beginning in 2004.



Regional/seasonal evaluation of isoprene emissions: Formaldehyde column measurements from space (GOME)



Abbot, D., P. Palmer, R. Martin, K. Chance, D. Jacob, A. Guenther, Seasonal and interannual variability of isoprene emissions as determined by formaldehyde column measurements from space, *Geo. Res. Lett.*

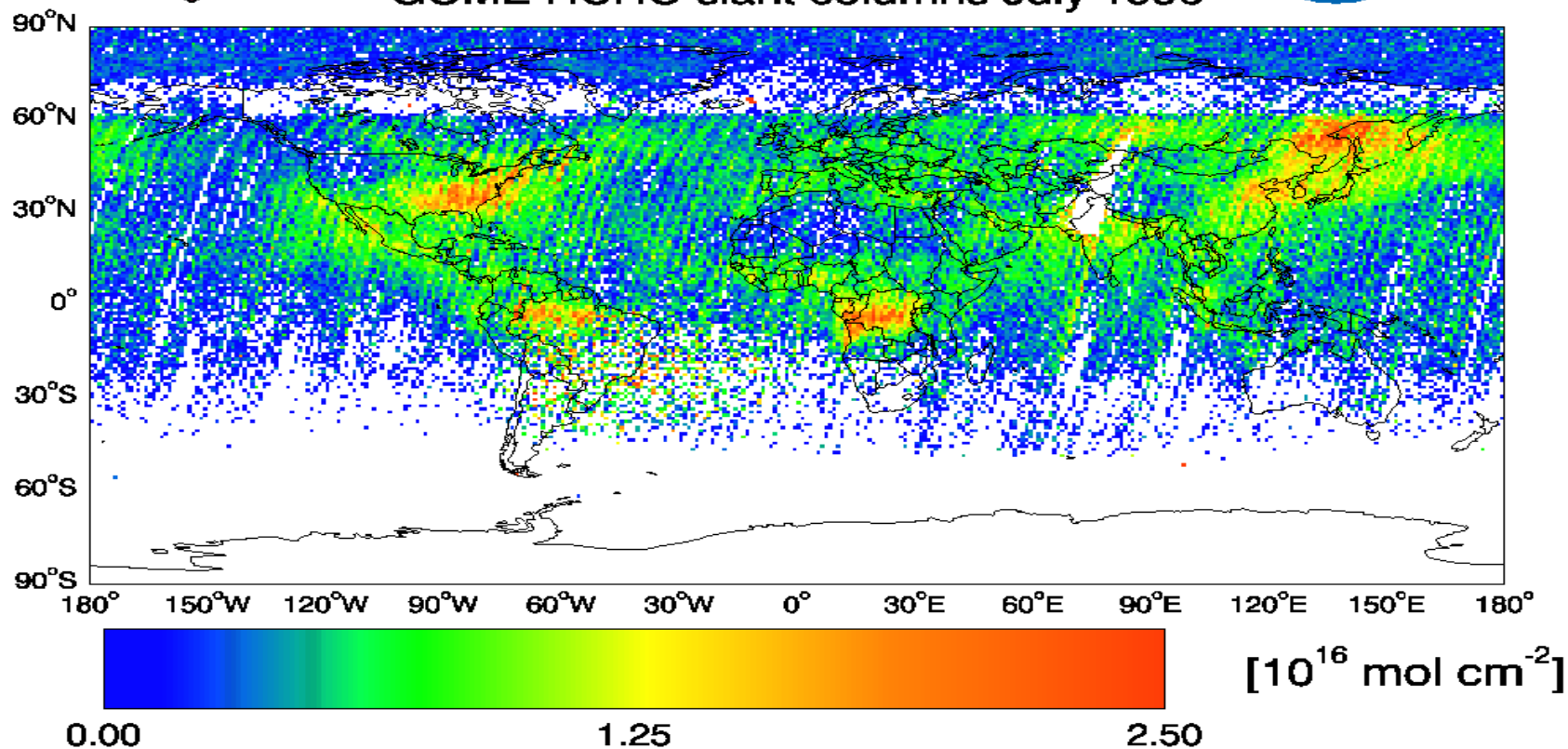
Can we evaluate isoprene emissions for all regions and seasons using remote sensing of HCHO ?



Palmer et al. 2003



GOME HCHO slant columns July 1996



Very difficult in the tropics.

Summary and Acknowledgements

Summary

- Leaf, canopy, landscape and regional flux tools are needed to develop and evaluate regional biogenic VOC emission models
- There have been considerable advancements in methods on all scales
- We have a reasonable suite of tools and expect further improvements

Collaborators

United States: Chris Geron, Tom Pierce, Brian Lamb, Hal Westberg, Dorian Abbot, Paul Palmer, Daniel Jacob, Randall Martin, Paul Shepson, Ray Fall

Europe: Markku Kulmala, Michael Boy, Paasi Aalto

Brazil: Paulo Artaxo, Luciana Gatti, Oscar Vega, Carla Trostorf

Sponsors

The National Science Foundation

U.S. Environmental Protection Agency

National Aeronautics and Space Administration