Biogenic Volatile Organic Compounds in the Atmosphere
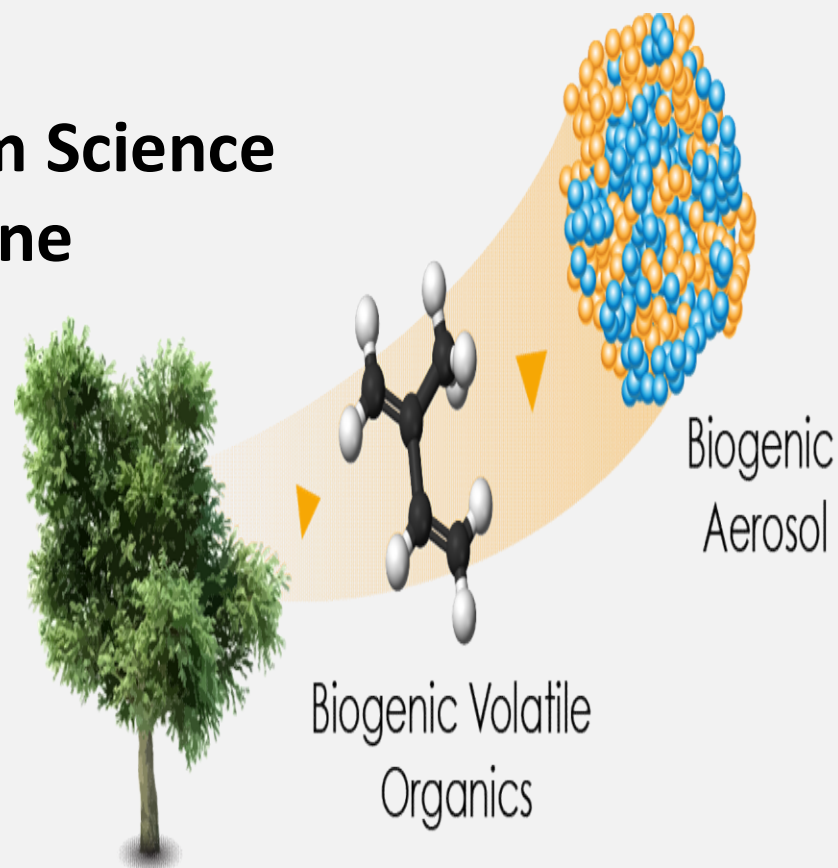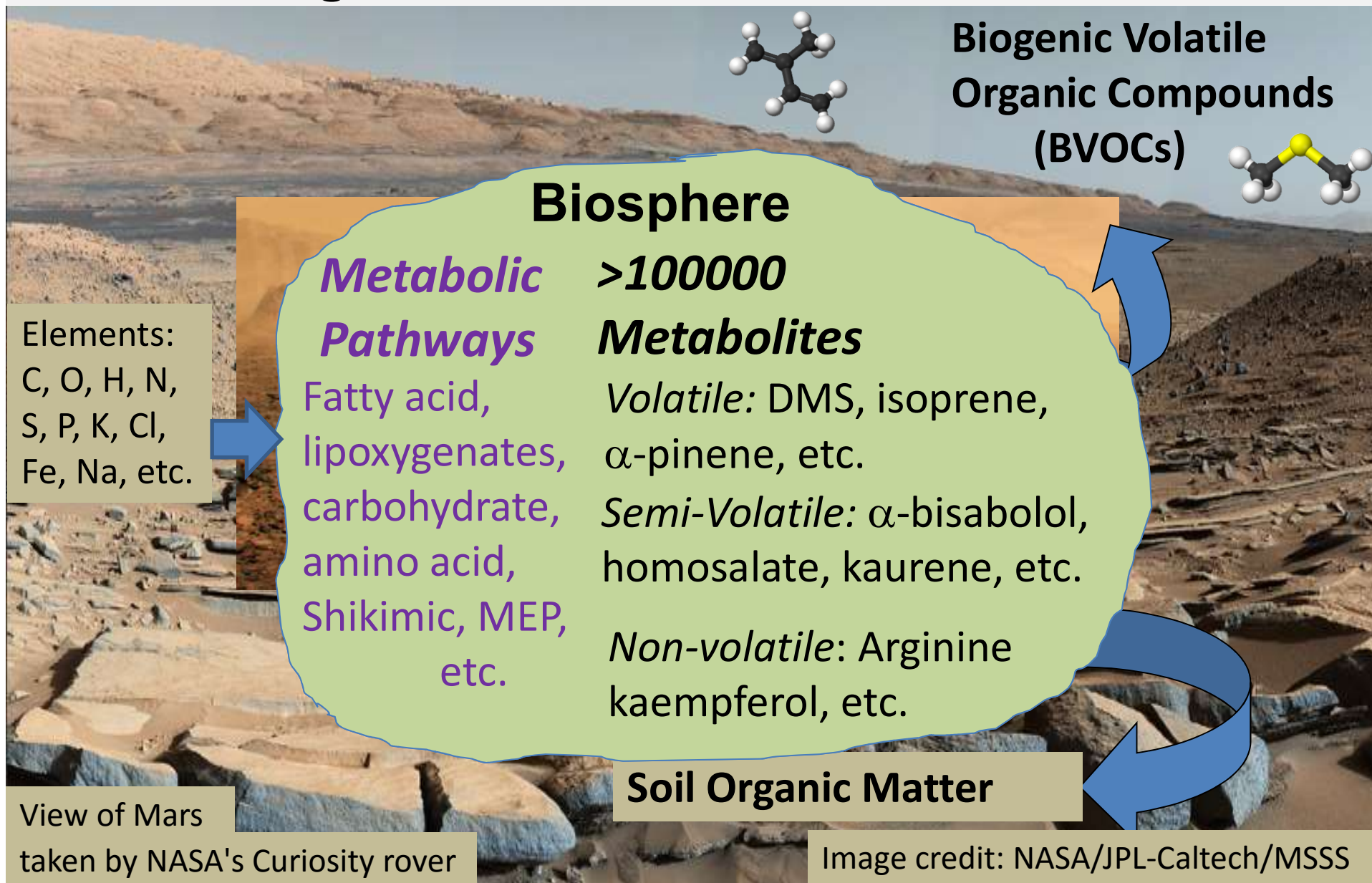
Alex Guenther

Department of Earth System Science
University of California, Irvine
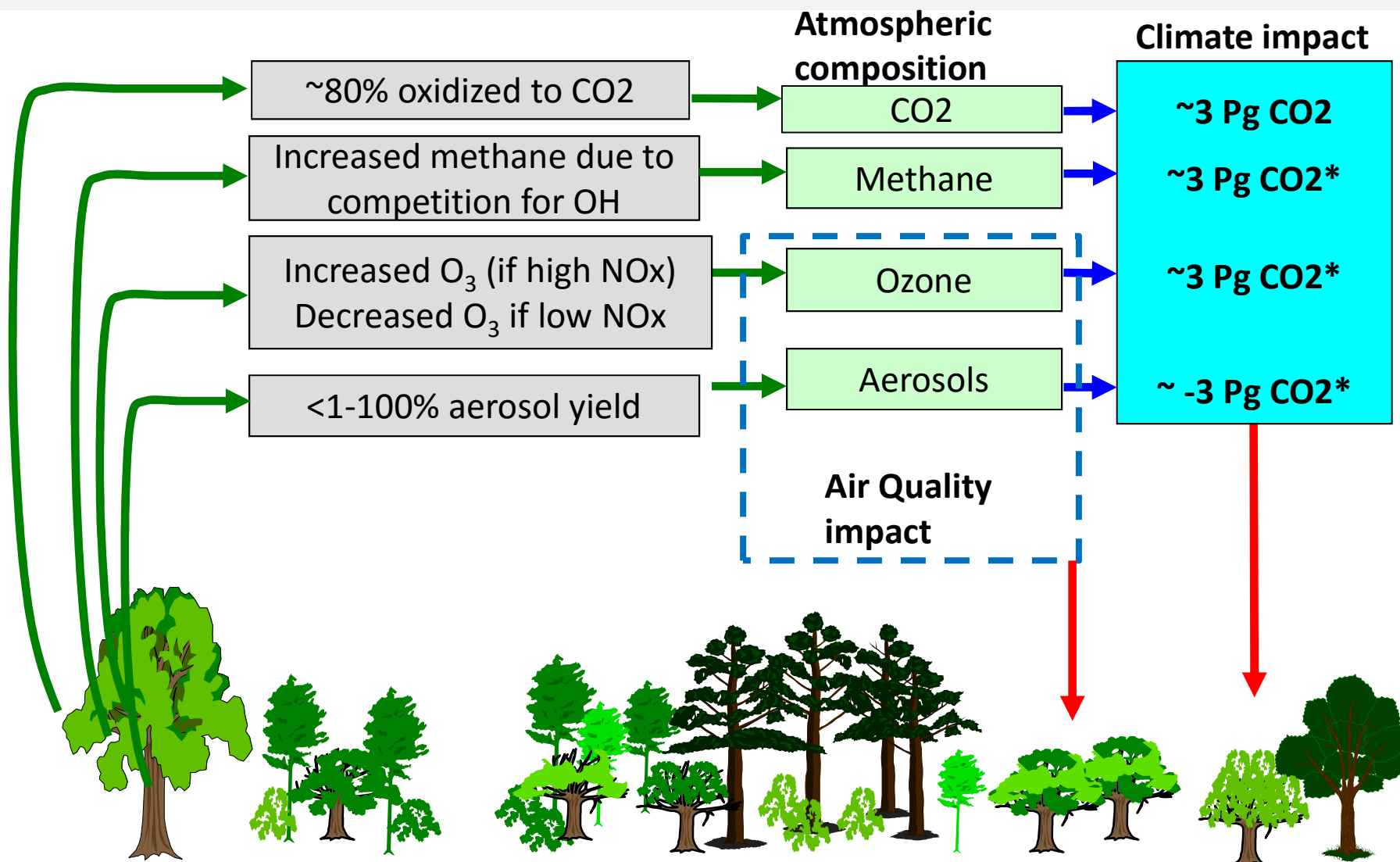
NEMC, August 8, 2016

Biogenic Aerosol

Biogenic Volatile Organics

Volatile Organics in the Atmosphere: chemical signature of life

Biogenic Volatile Organic Compounds (BVOCs)

Biosphere

Elements: C, O, H, N, S, P, K, Cl, Fe, Na, etc.

Metabolic Pathways

Fatty acid, lipoxygenates, carbohydrate, amino acid, Shikimic, MEP, etc.

>100000 Metabolites

Volatile: DMS, isoprene, α-pinene, etc.

Semi-Volatile: α-bisabolol, homosalate, kaurene, etc.

Non-volatile: Arginine kaempferol, etc.

Soil Organic Matter

View of Mars taken by NASA's Curiosity rover

Image credit: NASA/JPL-Caltech/MSSS

BVOC emissions impact on the Earth System: Air quality and climate

Atmospheric composition

~80% oxidized to CO2	CO2
Increased methane due to competition for OH	Methane
Increased O_3 (if high NOx) Decreased O_3 if low NOx	Ozone
<1-100% aerosol yield	Aerosols

Air Quality impact

Climate impact

~3 Pg CO2

~3 Pg CO2*

~3 Pg CO2*

~ -3 Pg CO2*

*Global warming potential (GWP): ratio of time-integrated radiative forcing of 1 Tg VOC compared with 1 Tg CO2 over 100 year time horizon (Collins et al. 2002)

Guenther et al. 2005

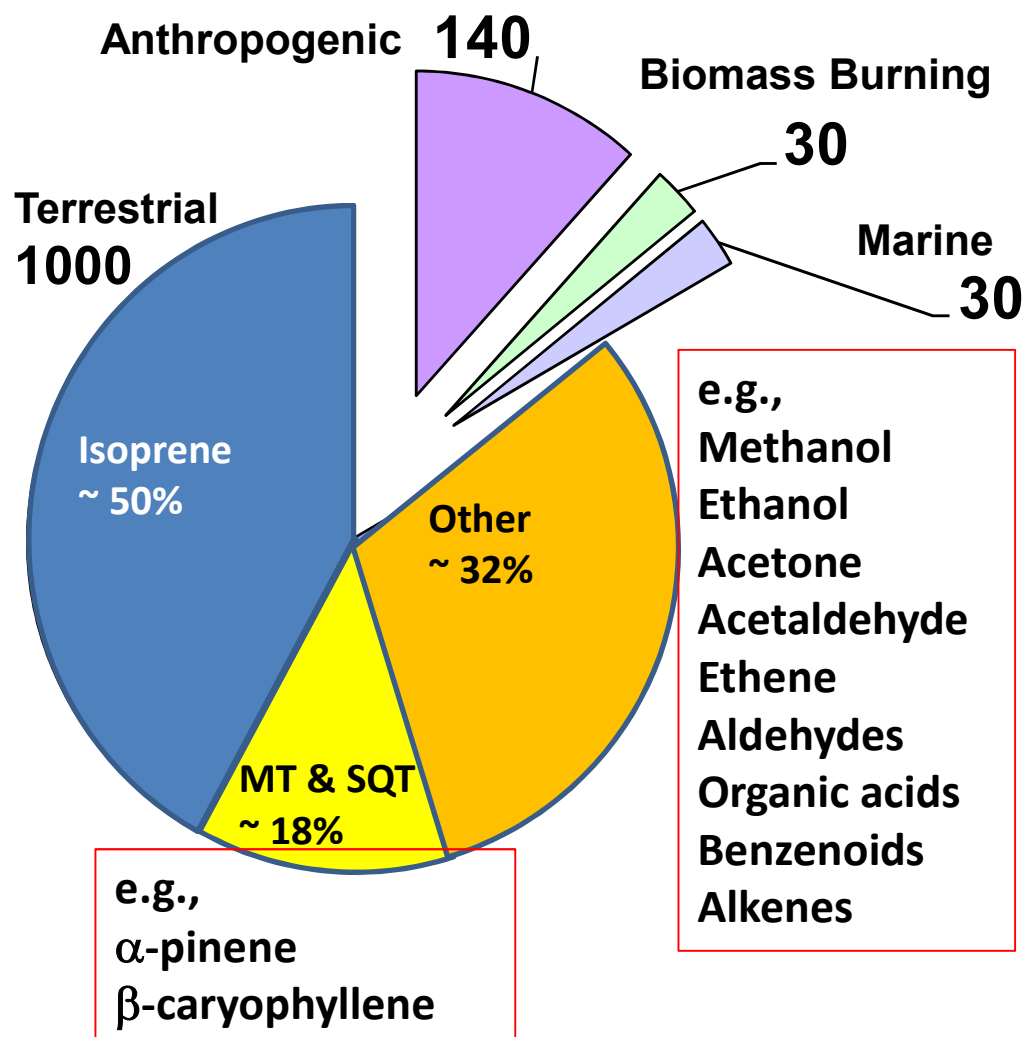# A brief history of BVOC emissions and Climate System and Air Quality modeling

Rasmussen, APCA 1972: "What do the hydrocarbons from trees contribute to air pollution?"

NAS 1989: "The combination of biogenic VOCs with anthropogenic NOx can have a significant effect on photochemical ozone formation"

Prevailing Opinion:

Went, Nature 1960 hypothesis: plant volatiles "play a very important role in the heat balance of the Earth"

Altshuller AE 1983: "natural hydrocarbons do NOT contribute substantially to the formation of either ozone or aerosols in ambient air"

IPCC AR3 (2001): Accurate estimates of greenhouse gases requires accurate BVOC emissions.

IPCC AR4 (2007): Accurate estimates of aerosols requires accurate BVOC emissions.

1960   1970   1980   1990   2000   2010

Climate System Models (CSMs) and Air Quality Models (AQMs)

First CSMs

First CSMs with BVOCs

BVOC emission models:

First AQMs

First AQMs w/BVOC

17 landcovers 4 compounds

>300 plant types 15 PFTs 146 compounds

BVOC dominate total VOC flux into the atmosphere

>25,000 organic compounds identified in plants, but many are not volatile

146 BVOC are included in MEGAN2.1

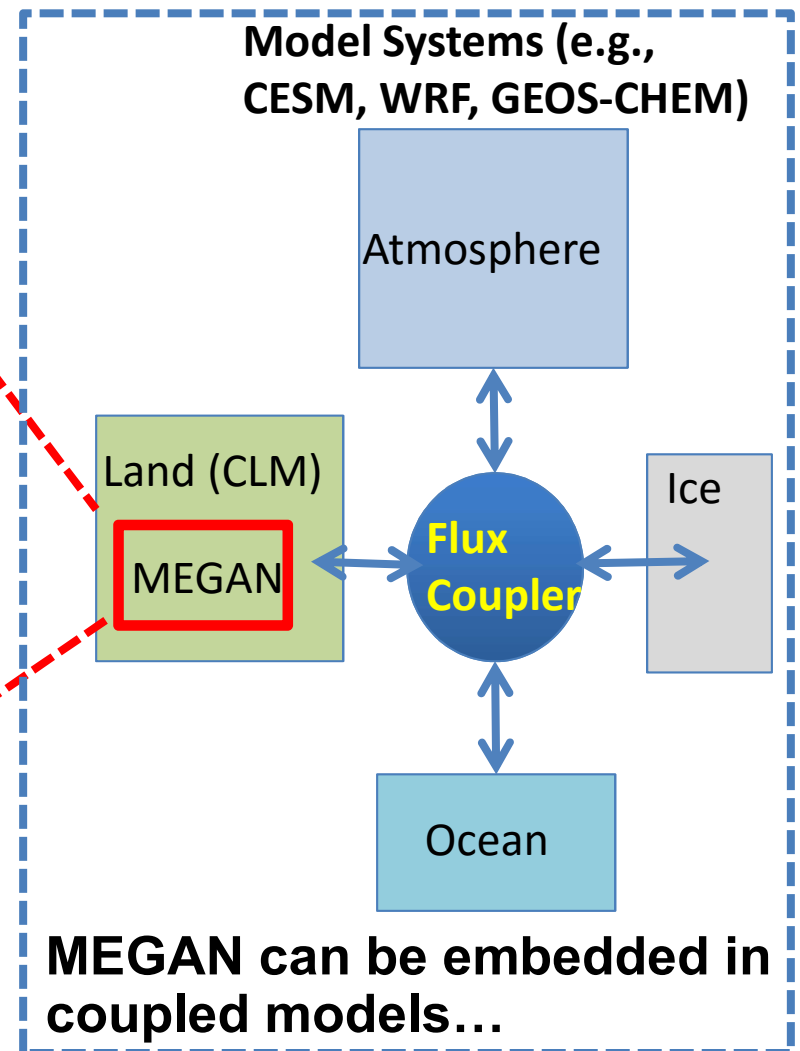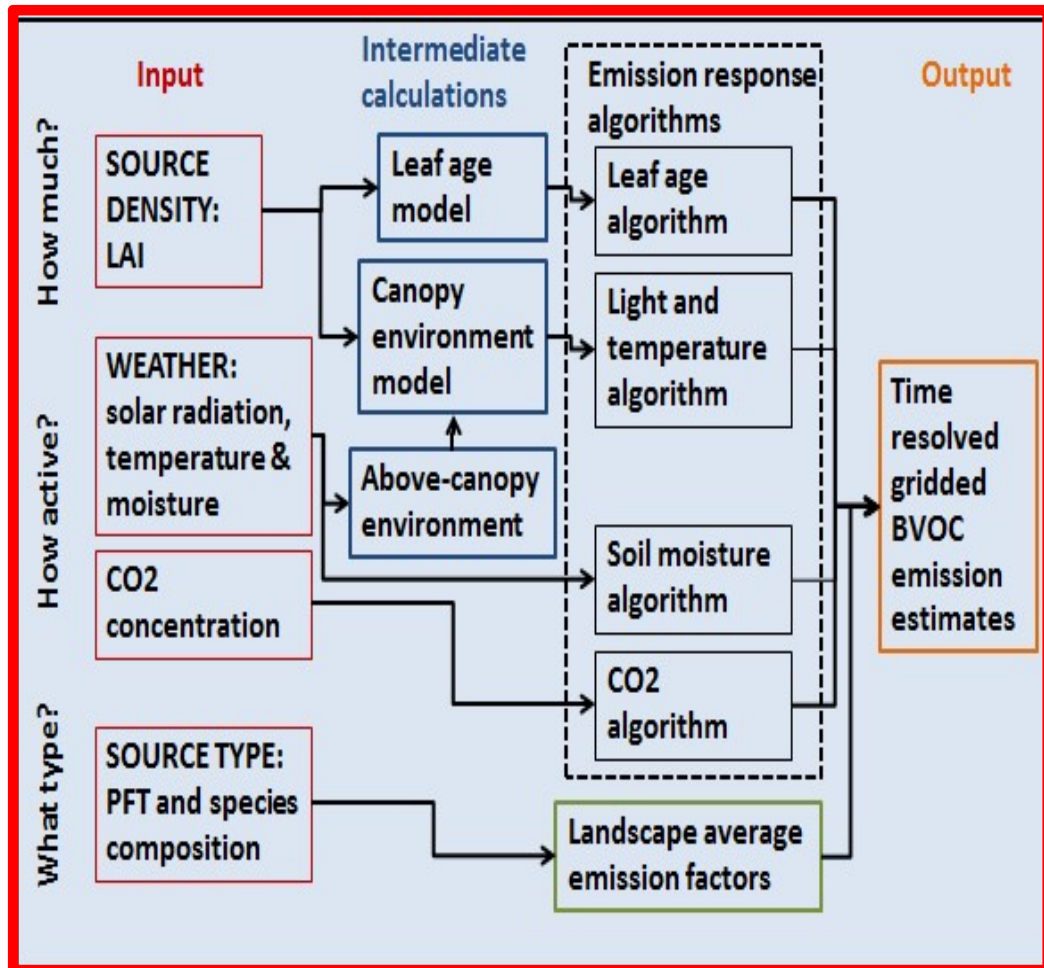10 BVOC comprise ~80% of the total VOC flux estimated with MEGAN2.1

Anthropogenic **140**

Biomass Burning **30**

Marine **30**

Terrestrial **1000**

Isoprene ~ 50%

Other ~ 32%

MT & SQT ~ 18%

e.g.,
Methanol
Ethanol
Acetone
Acetaldehyde
Ethene
Aldehydes
Organic acids
Benzenoids
Alkenes

e.g.,
α-pinene
β-caryophyllene

Global Annual Emission (Tg)
Sources: Guenther et al. 2012 and EDGAR

Quantitative BVOC emission models are now widely used in Climate and Air Quality modeling systems

Model of Emissions of Gases and Aerosols from Nature (MEGAN) Guenther et al. 2012

Model Systems (e.g., CESM, WRF, GEOS-CHEM)

Atmosphere

Land (CLM)

MEGAN

Flux Coupler

Ice

Ocean

MEGAN can be embedded in coupled models…

or run as a "stand-alone" model

Quantifying air quality and climate impacts of changing BVOC emissions
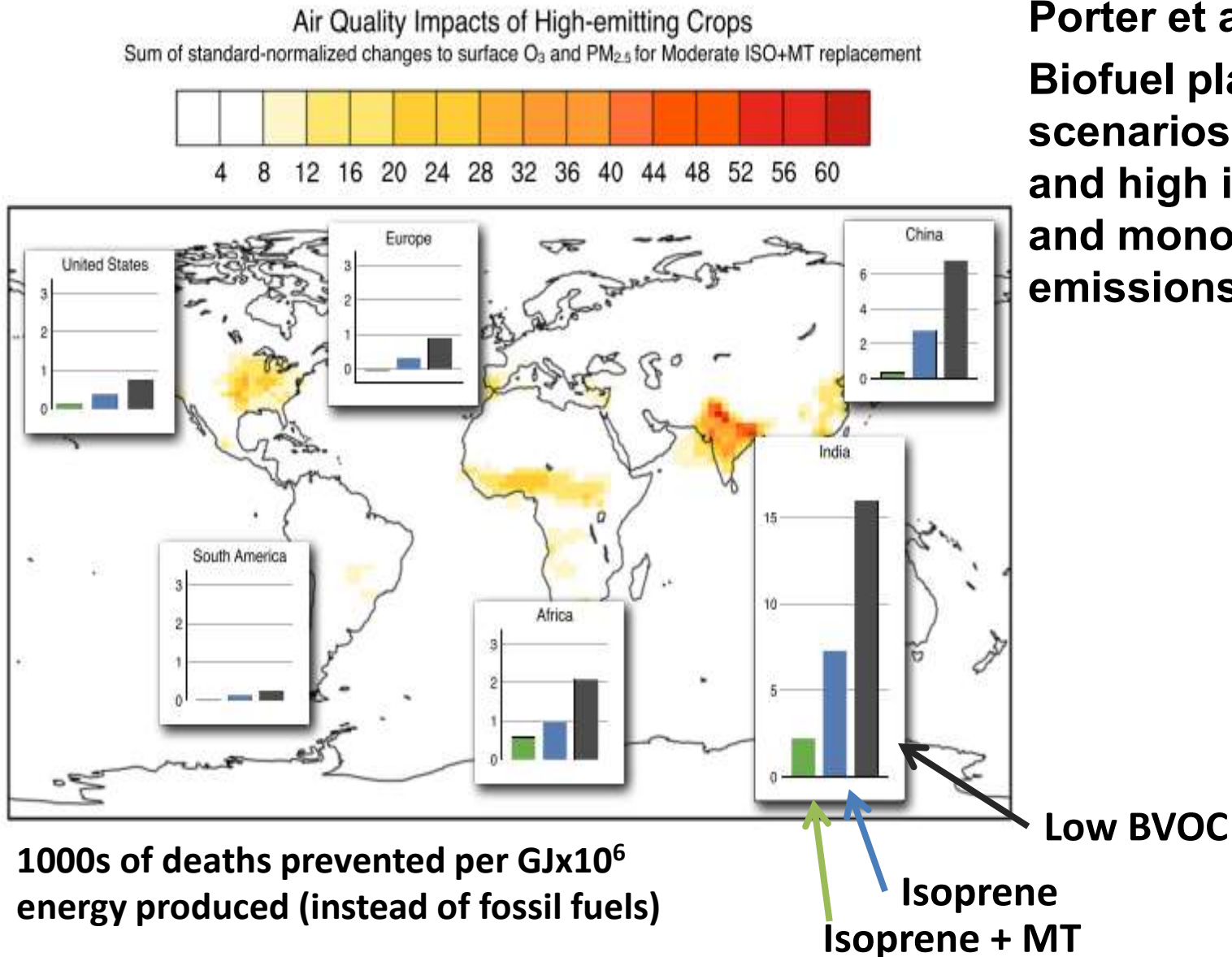
Air Quality Impacts of High-emitting Crops
Sum of standard-normalized changes to surface O_3 and $PM_{2.5}$ for Moderate ISO+MT replacement

4 8 12 16 20 24 28 32 36 40 44 48 52 56 60

United States
Europe
China
South America
India
Africa

Porter et al. 2015:

**Biofuel plantation scenarios including low and high isoprene (ISO) and monoterpene (MT) emissions**

Low BVOC

Isoprene

Isoprene + MT

1000s of deaths prevented per GJx10^6 energy produced (instead of fossil fuels)

Quantifying air pollution and climate impacts of changing BVOC emissions

Porter et al. 2015:

Biofuel plantation scenarios including low and high isoprene (ISO) and monoterpene (MT) emissions

BVOC emission models have advanced through multi-scale observations

Accurate air quality and climate models

Global earth system

Regional: interactions of emissions, dynamics, chemistry

Canopy: micro-environment, BVOC fate

Cellular: Enzyme activity, electron transport

Fundamental understanding
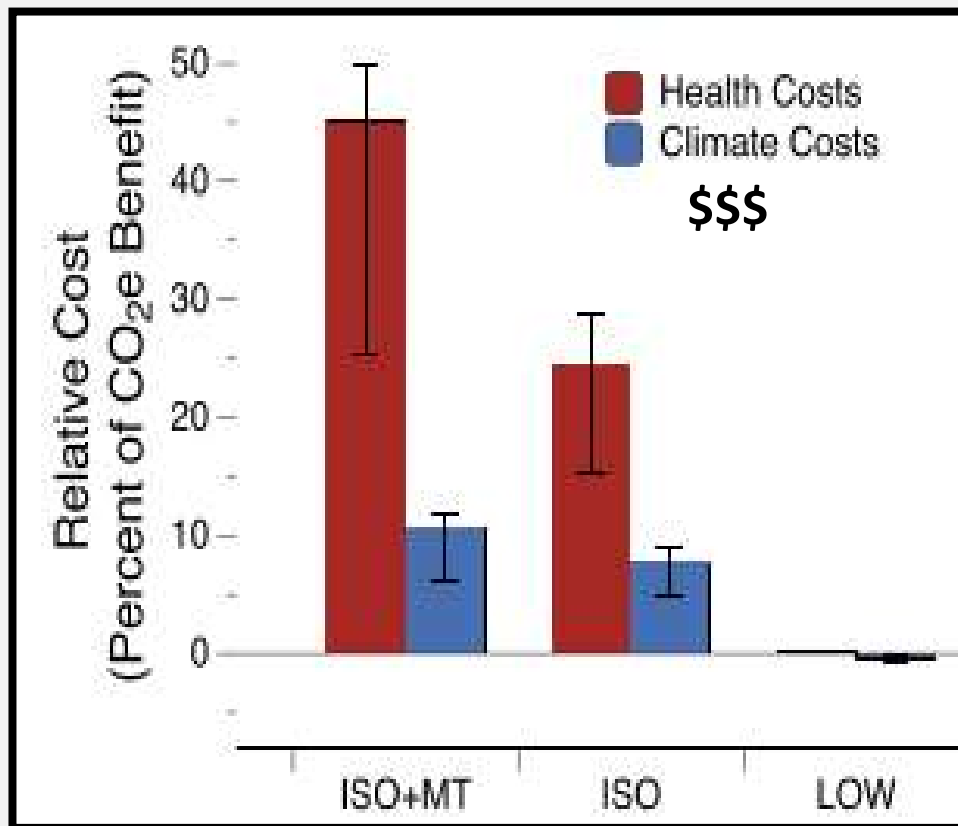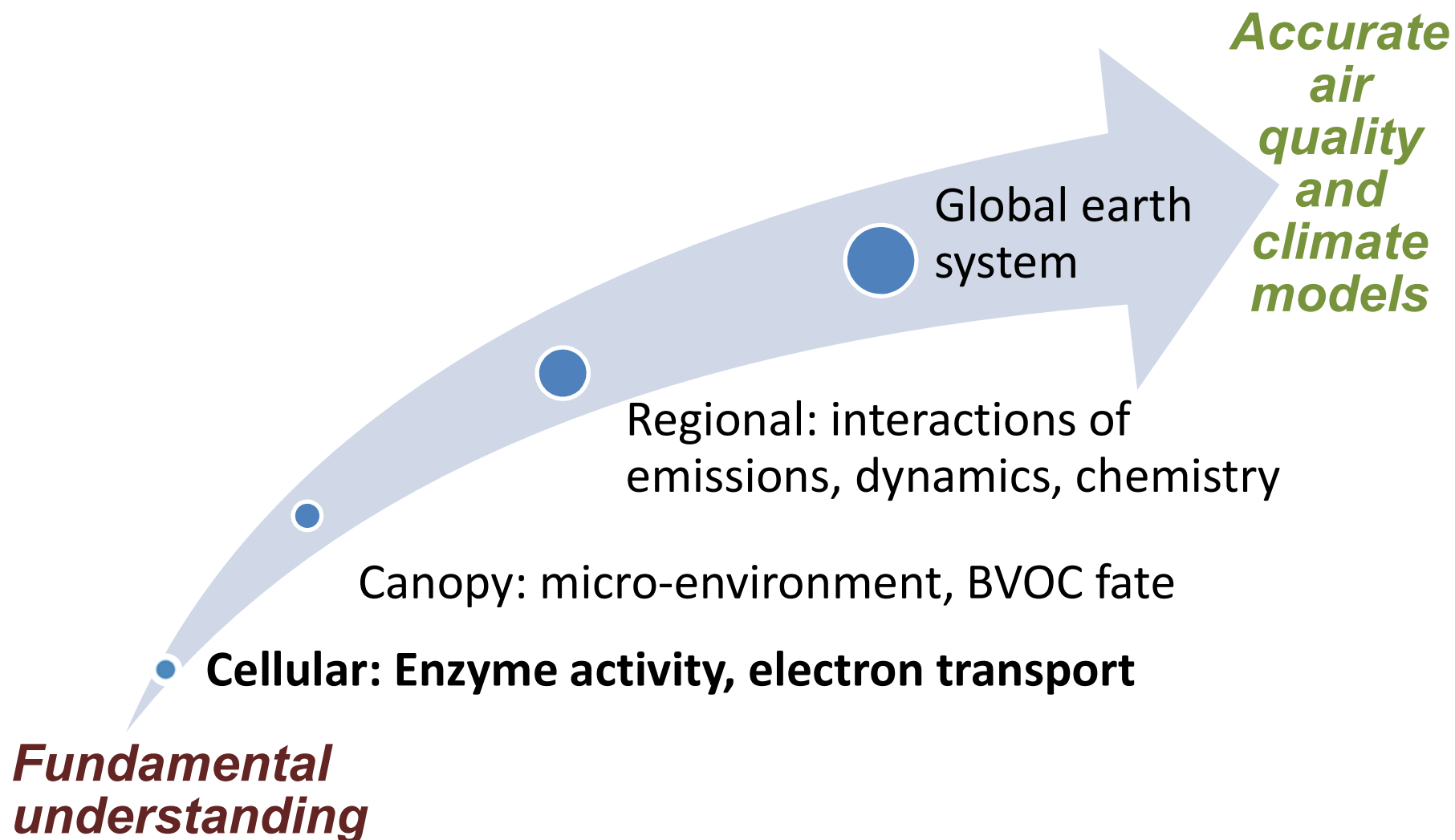
MEGAN uses simple mechanistic algorithms to simulate key processes controlling biogenic emissions
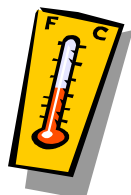
Temperature (Leaf-level)
Instantaneous and past (24 hrs, 10 days)
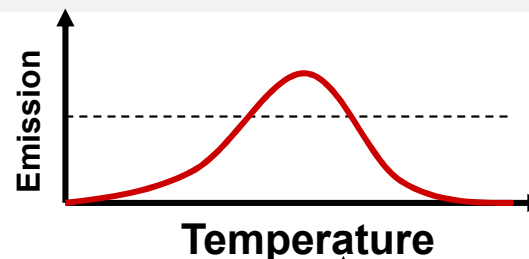
Light: Photosynthetic Photon Flux Density (PPFD)
Instantaneous and past (24 hrs and 10 days)
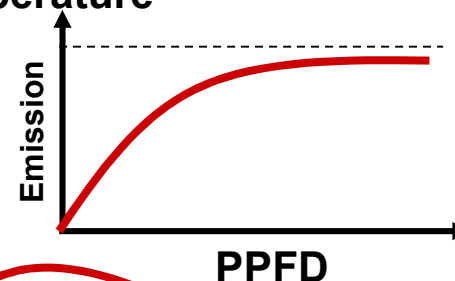
Soil Moisture
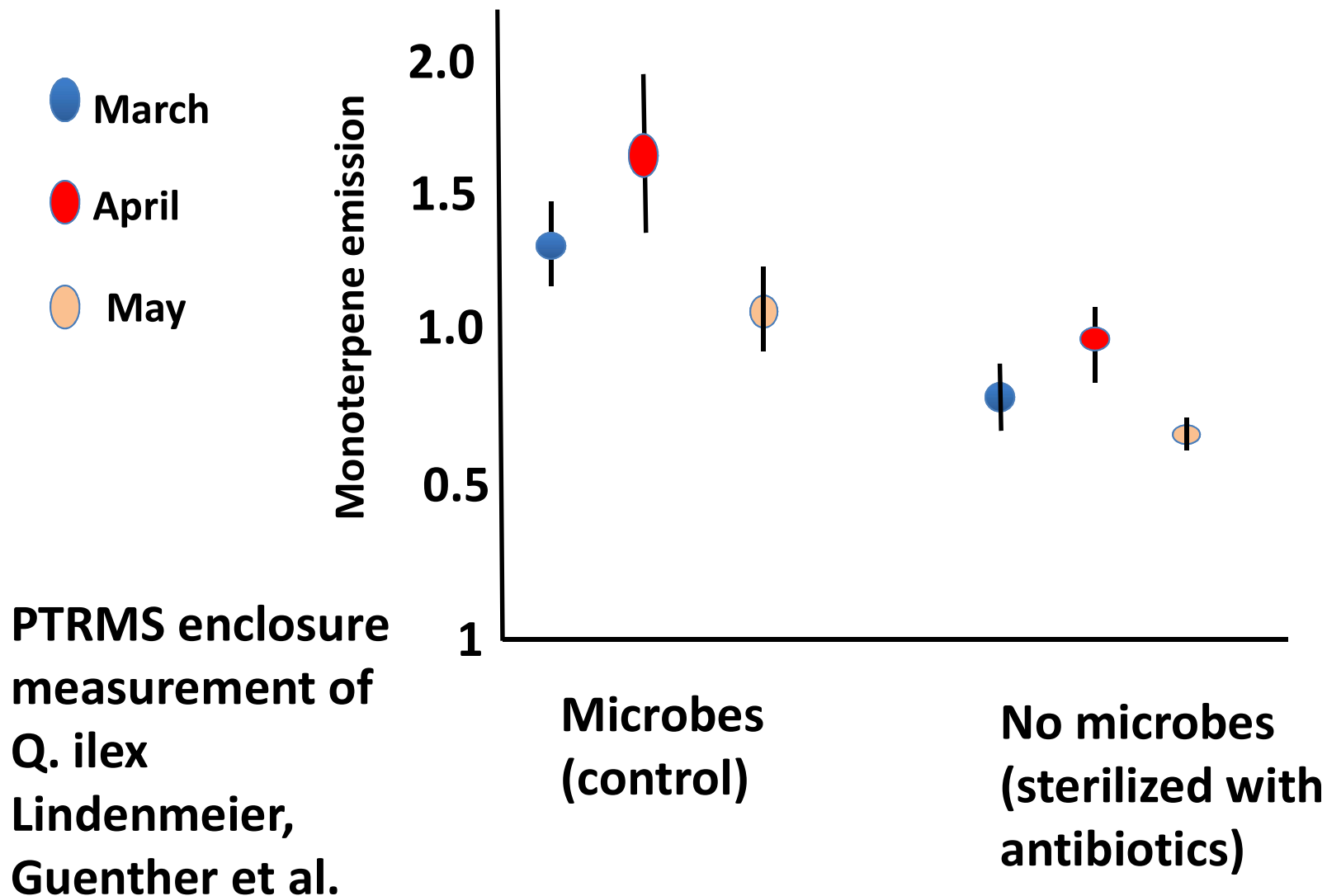**Initial increase with reduced transpiration; eventually a decrease**
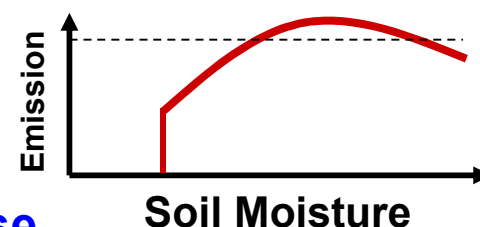
Leaf Age and Area
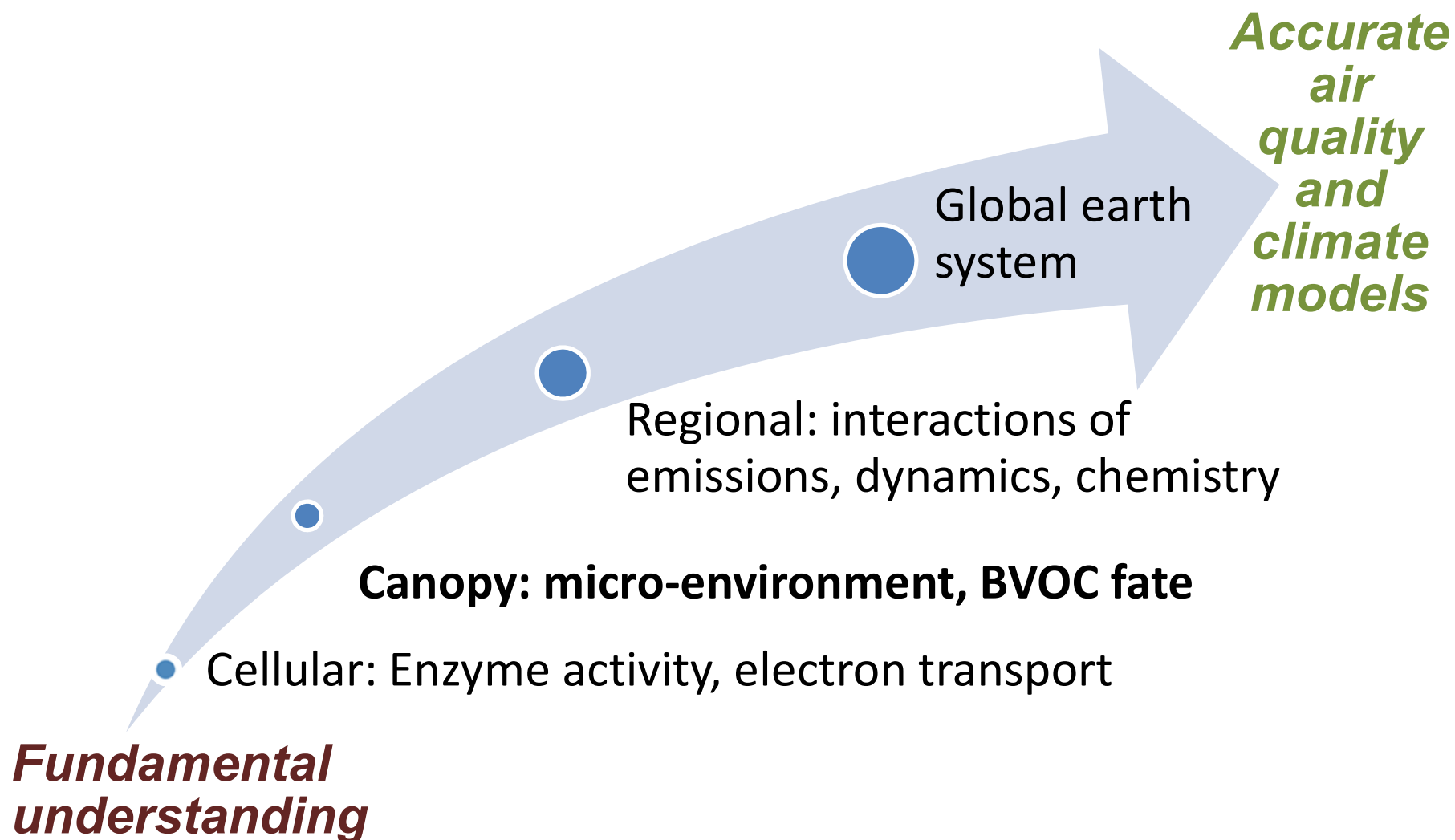**Age response varies; Leaf area increases emissions**
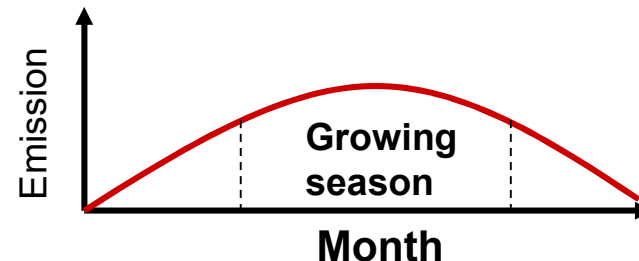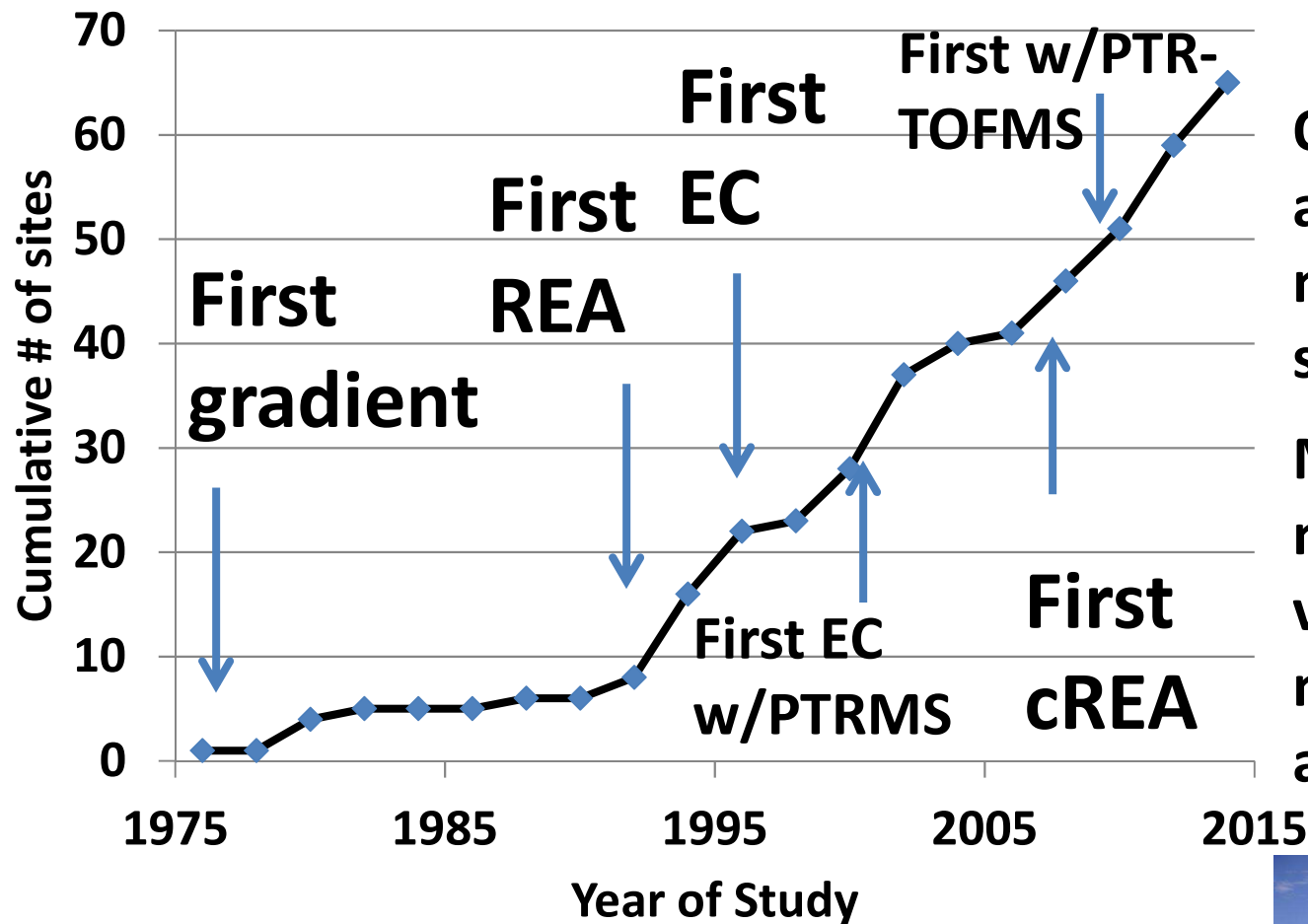
Carbon dioxide
Decrease with increasing CO2.

Guenther et al. 1991, 1995, 1999, 2006, 2012

10
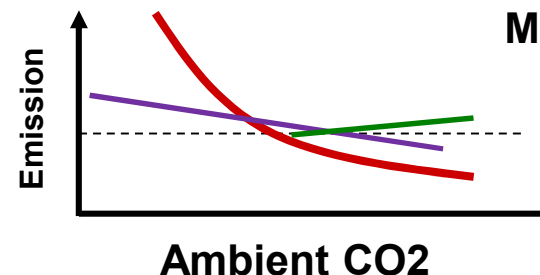
But we may be missing some processes:
For example, are leaf microbes important?

PTRMS enclosure measurement of Q. ilex Lindenmeier, Guenther et al.

Legend:
- March
- April
- May

Y-axis: Monoterpene emission (2.0, 1.5, 1.0, 0.5, 1)

X-axis categories:
- Microbes (control)
- No microbes (sterilized with antibiotics)

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Fundamental understanding

Whole canopy flux measurements: Evaluate, investigate long-term variations
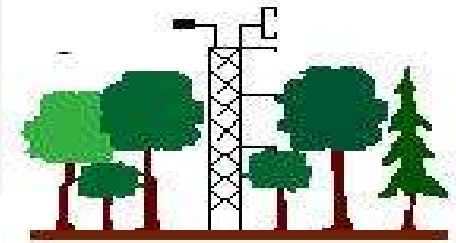
Observations tend to agree within 50% for models driven by site specific inputs.

Models can explain most of the temporal variation ($r^2 > 0.8$) at most sites but few are long-term

First gradient

First REA

First EC

First w/PTR-TOFMS

First EC w/PTRMS

First cREA

Cumulative # of sites vs **Year of Study**

EC: Eddy covariance
REA: Relaxed eddy accumulation
cREA: compact REA

Whole canopy flux measurements: Evaluate, investigate long-term variations

Missouri Ozarks AMERIFLUX flux tower May-Sept. 2011

Whole Ecosystem Isoprene
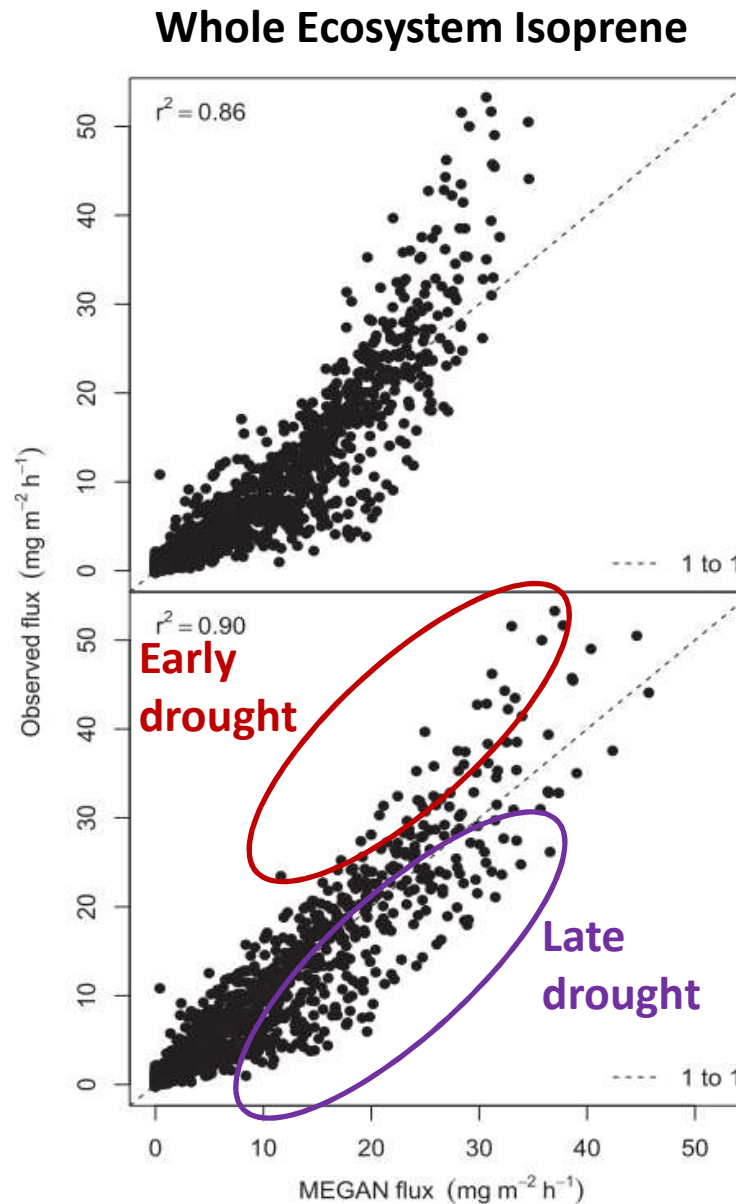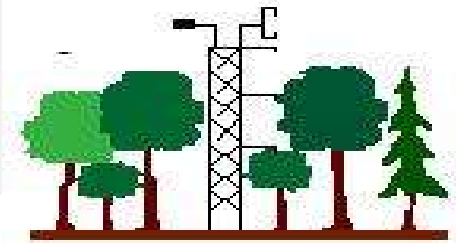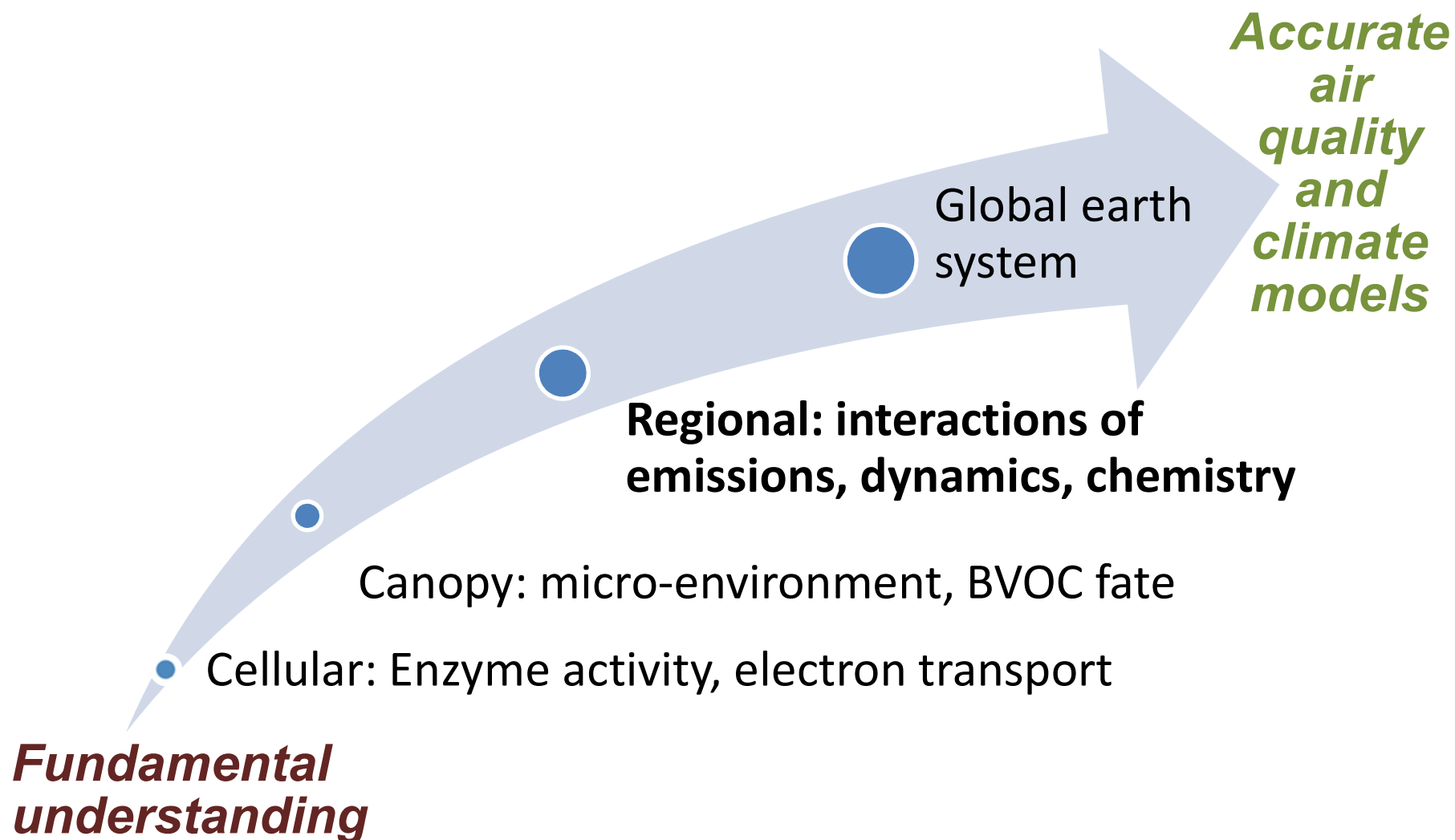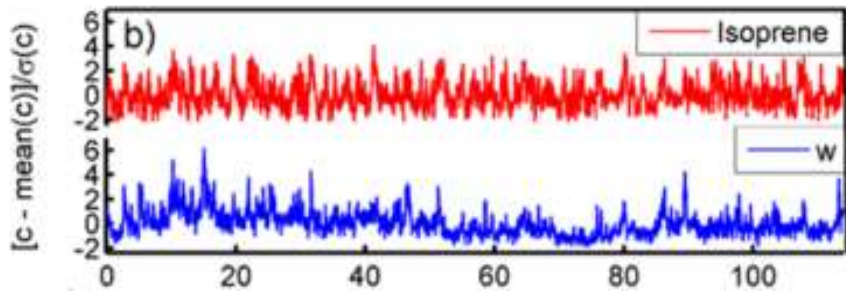

r² = 0.86 MEGAN (base algorithms)

r² = 0.9 MEGAN (acclimation algorithm)

Potosnak et al., 2014

14

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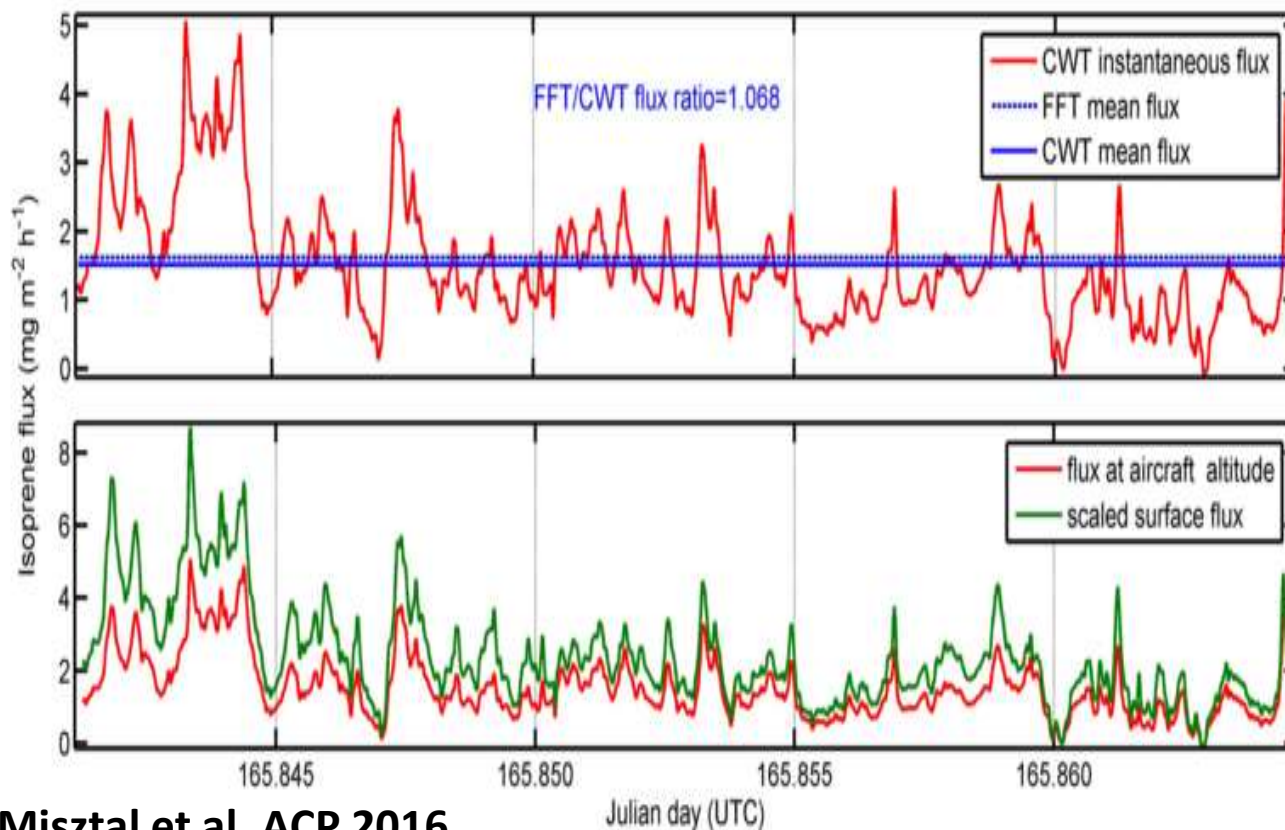
Fundamental understanding

Airborne PTRMS eddy covariance measurements

1. Fast response isoprene and vertical wind data

$$F = \overline{w'c'}$$

2. Calculate flux using wavelet approach with spatial resolution of ~ 2km

3. Adjust for flux divergence between surface and aircraft height

Misztal et al. ACP 2016

Airborne PTRMS eddy covariance measurements

30 m isoprene emission factors
(based on land cover, μg/m²/h)

High : 23611

Low : 0

● 2 km averaged isoprene data

▭ half-dome

Yu et al. in preparation

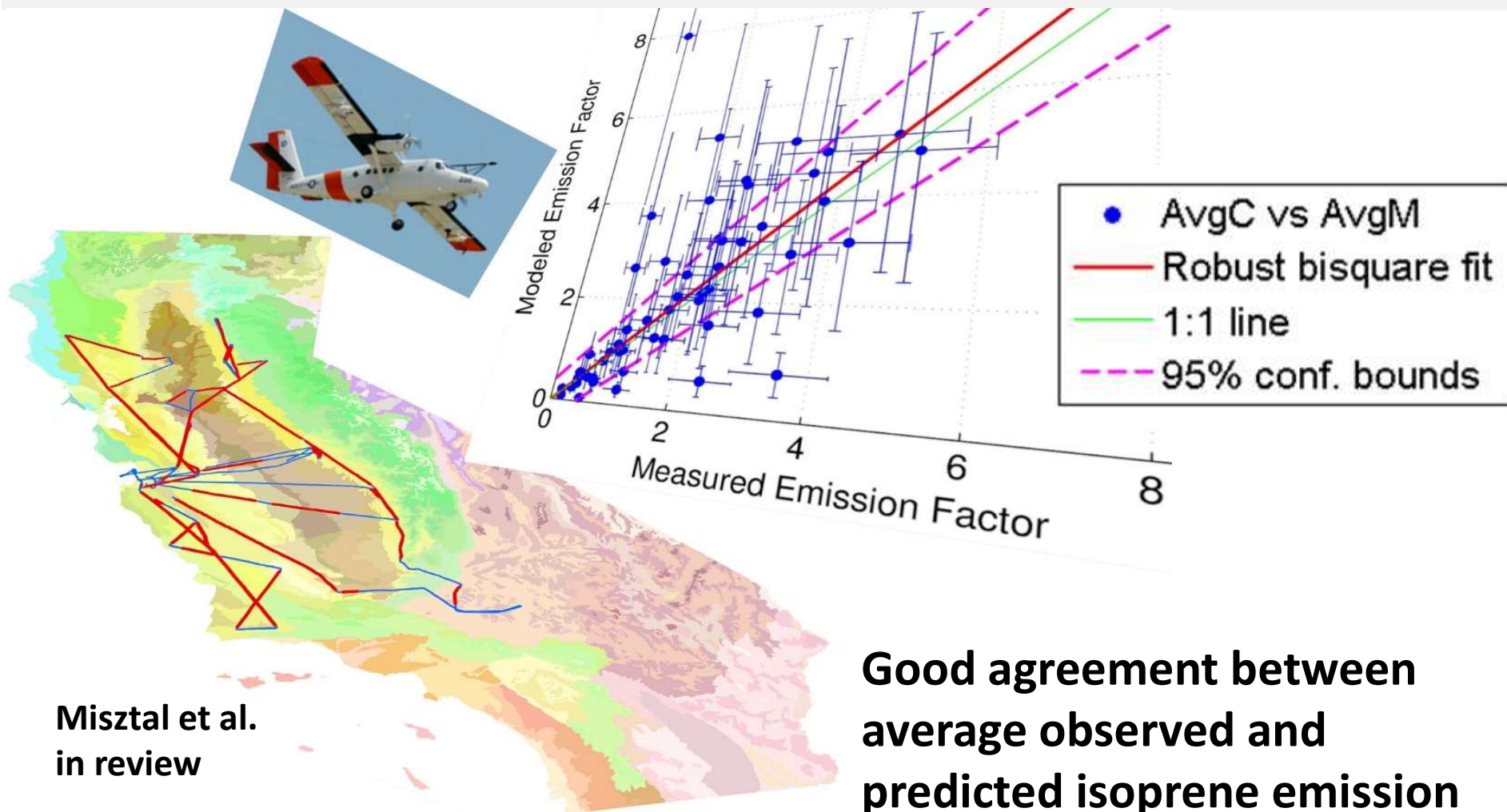4. Calculate "half dome footprint" based on altitude, wind speed and direction

Similar results (average isoprene emission for different for vegetation types) for 2km, 4km, and 6km footprints
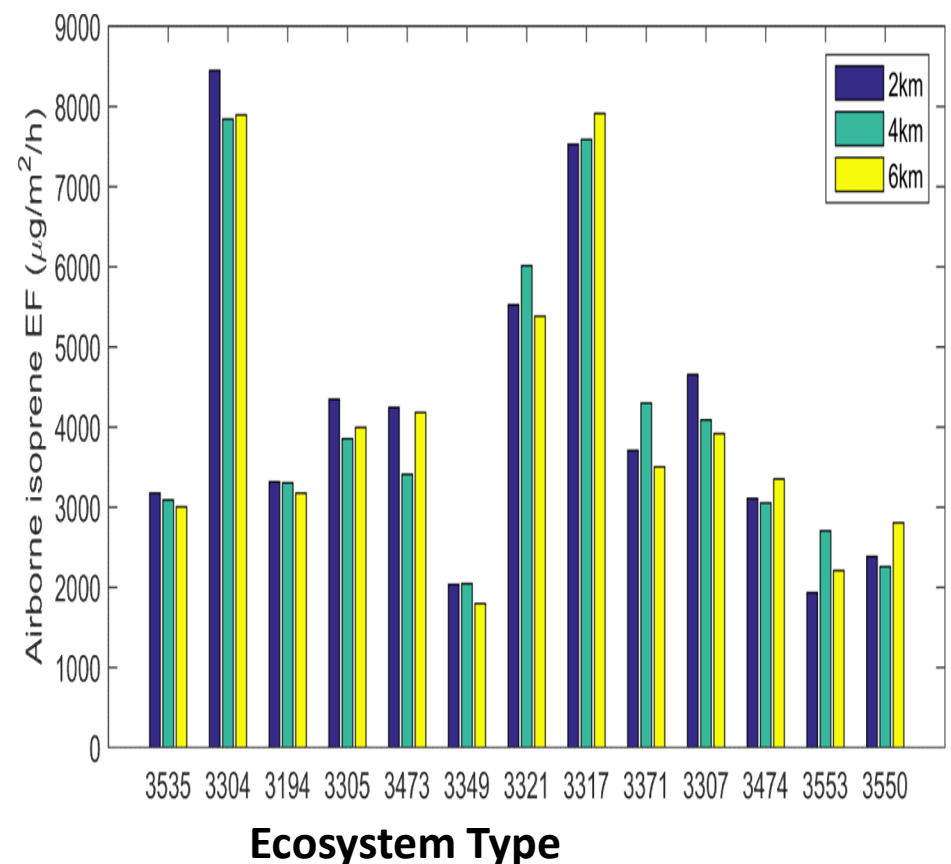
Aircraft EC-PTRMS evaluation of MEGAN model: Isoprene emission from California ecosystems
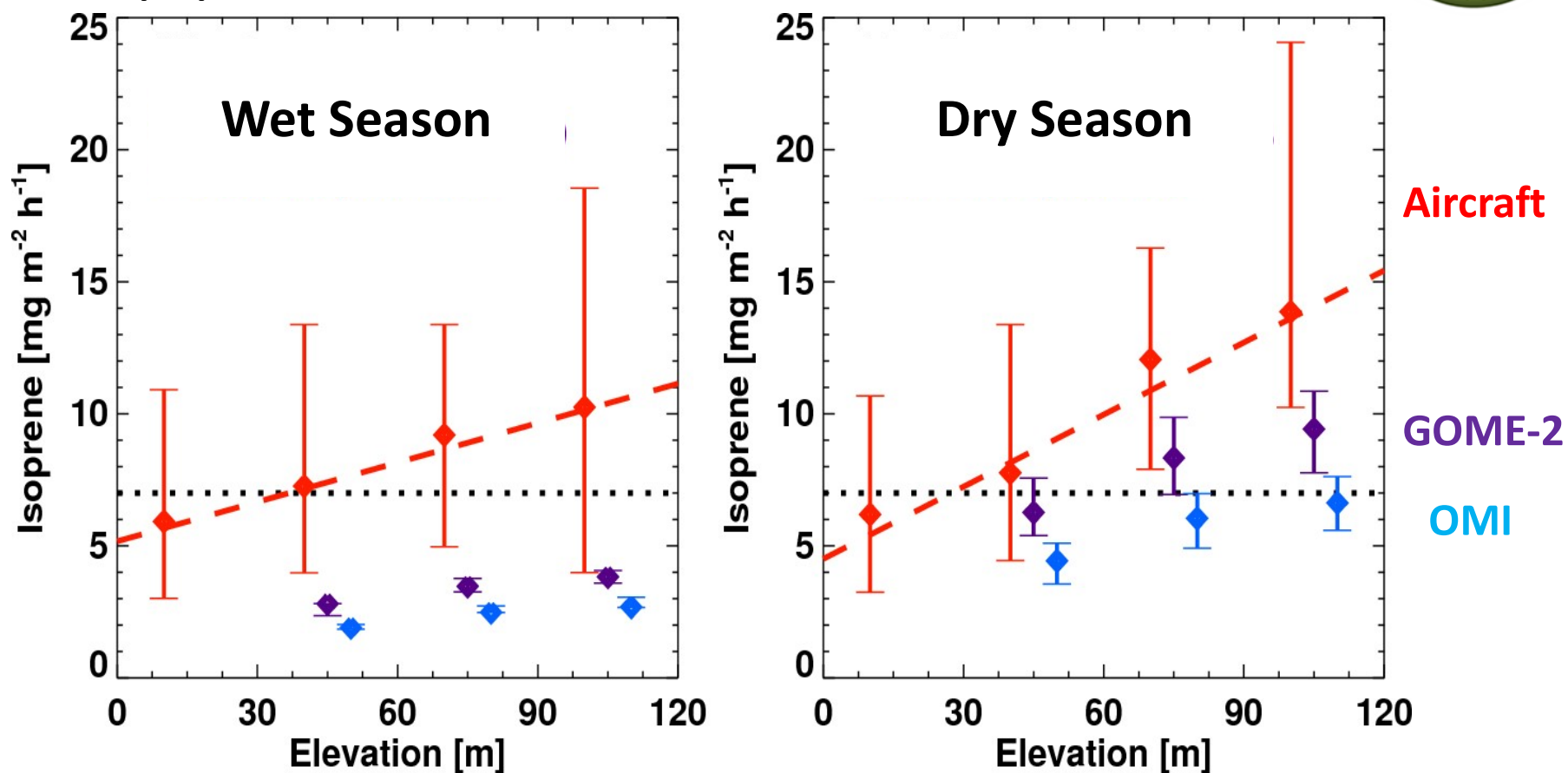

Misztal et al. in review

Good agreement between average observed and predicted isoprene emission for 48 California ecosystems
$r^2 = 0.79$, Slope = 1.09

Aircraft EC-PTRMS measurements reveal elevational gradient in Amazon isoprene emissions
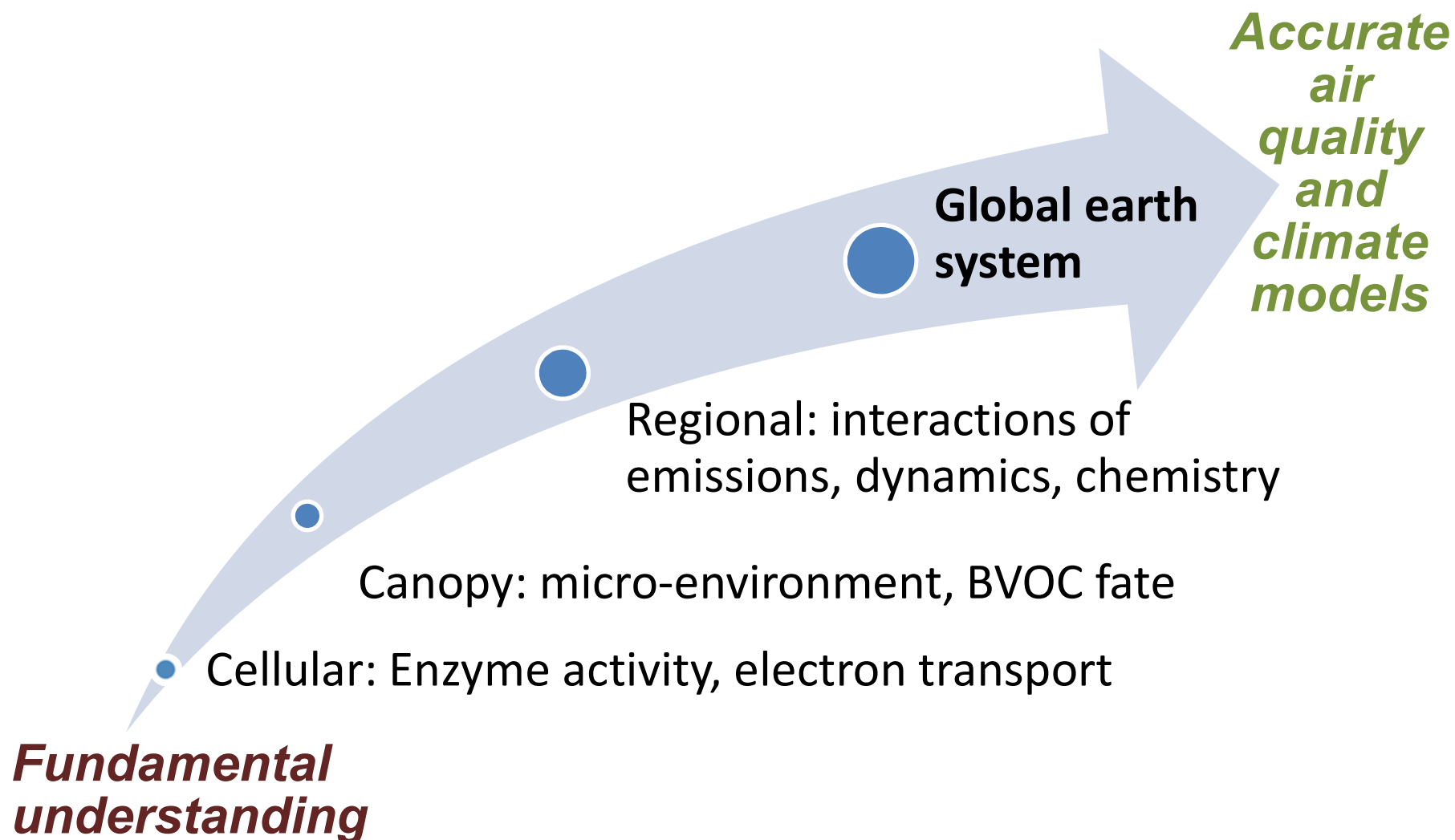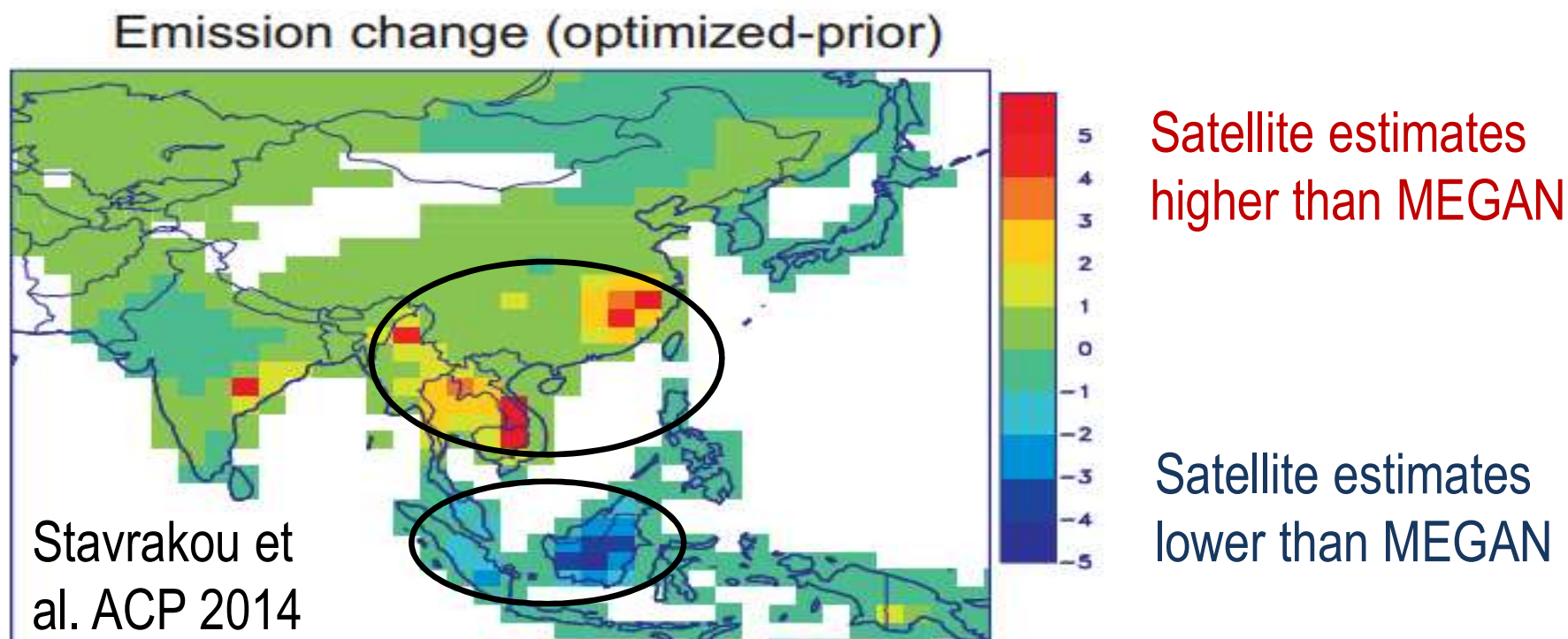
Gu et al. in preparation

Positive correlation between aircraft observed isoprene emissions and land surface elevation. This is supported by satellite observations- but the emission magnitude differs

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Fundamental understanding

Regional to global and seasonal to interannual variations of isoprene and methanol quantified using satellite data

Emission change (optimized-prior)

Satellite estimates higher than MEGAN

Satellite estimates lower than MEGAN

Stavrakou et al. ACP 2014

Satellite HCHO data indicates lower isoprene in Borneo and higher in Laos, E. China

- Recent measurements in SE Asia tropical forests indicates lower emissions. One family (non-emitters) dominates.
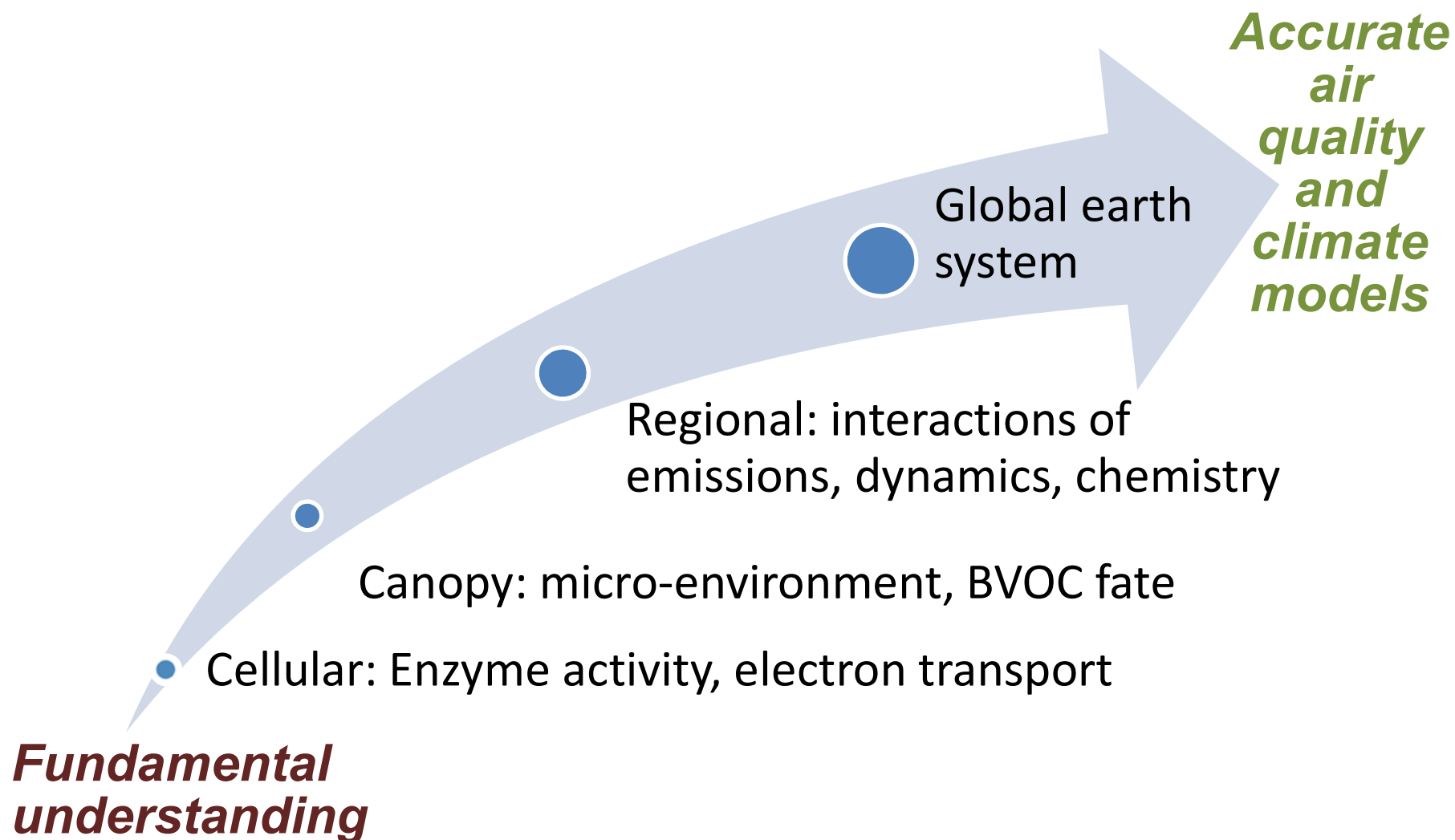- High isoprene plantations in E. China.

Can we detect isoprene from space?

Brauer et al. 2014
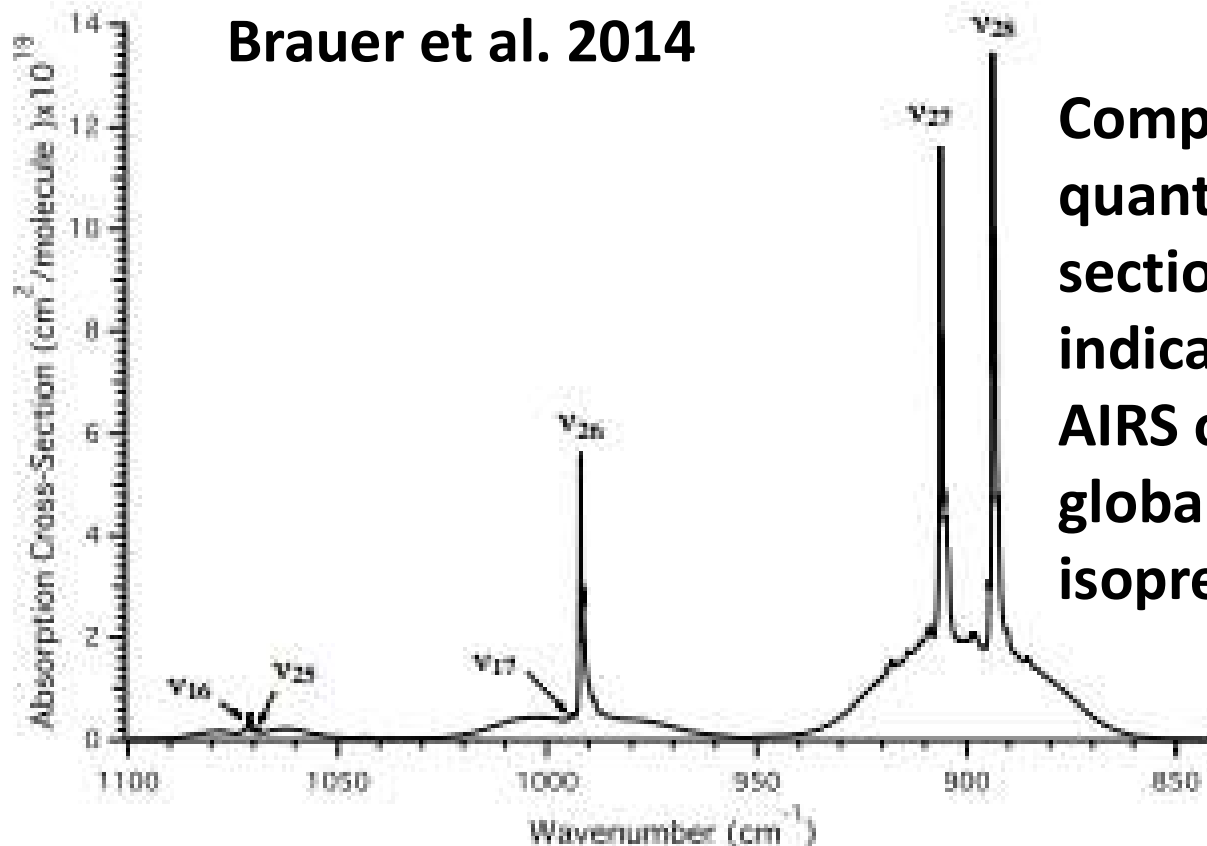
Comprehensive quantitative infrared cross sections of isoprene vapor indicate potential to use AIRS or IASI to observe global distribution of isoprene


Figure 5. Quantitative infrared spectrum of isoprene from 840 to 1100 cm^{-1} recorded at 298 K. Absorption cross sections are given in Naperian units (cm^2 molecule^{-1}) × 10^{19} for the composite spectrum recorded at 298 K.

Making progress towards measuring and modeling BVOC but may be missing some compounds and processes

Accurate air quality and climate models

Global earth system

Regional: interactions of emissions, dynamics, chemistry

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Cellular: Enzyme activity, electron transport

Fundamental understanding

Stress is an important driver of BVOC emission but is not adequately represented in models
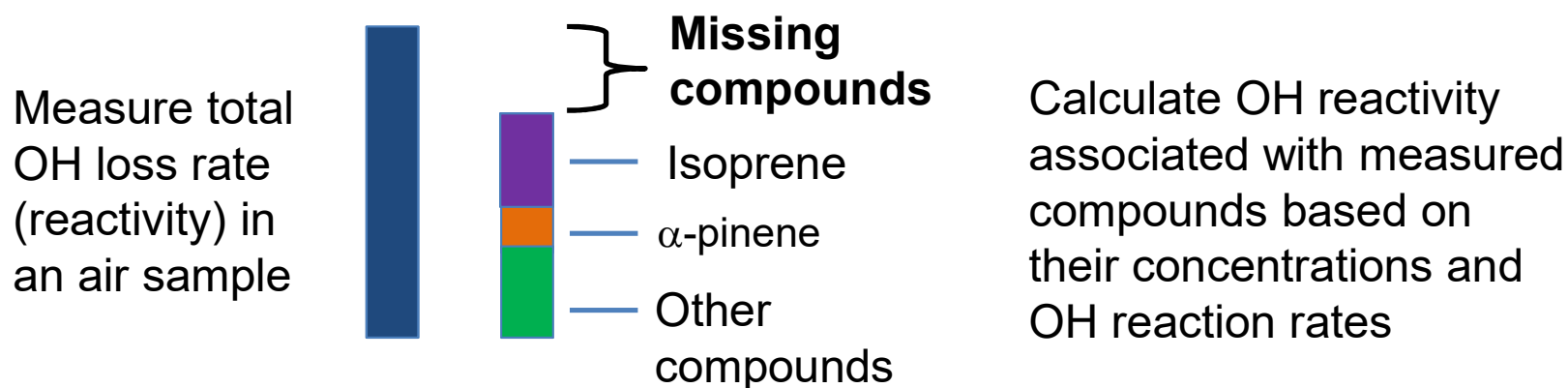
Whole ecosystem BVOC emission response to cold wave
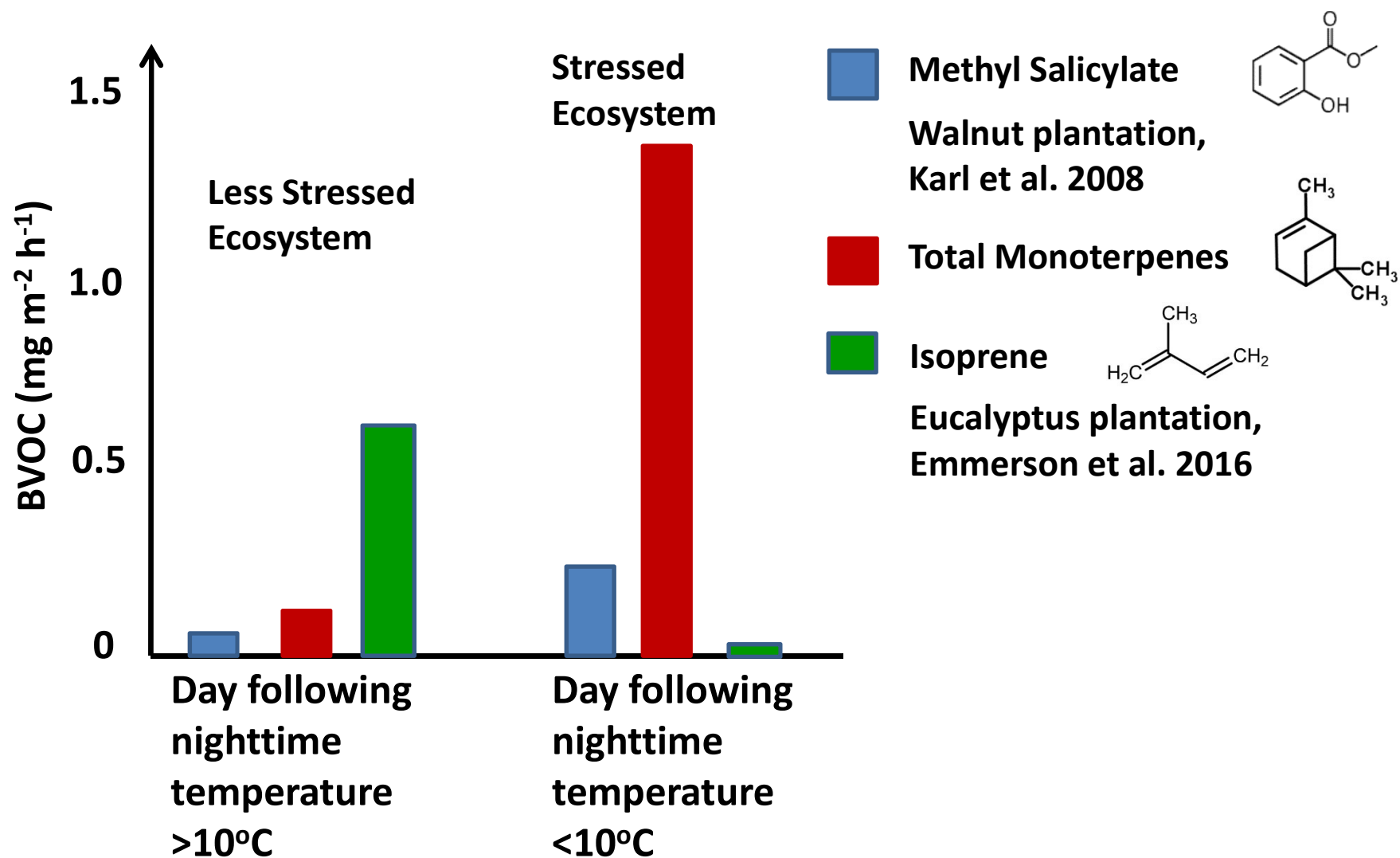
What are we missing?

Indirect approach: Identify what we are missing
-measure total loss or products by reaction with atmospheric reactants
-determine what can be accounted for by known compounds
-the remainder is what is missing

Measure total OH loss rate (reactivity) in an air sample

Missing compounds

Isoprene

α-pinene

Other compounds

Calculate OH reactivity associated with measured compounds based on their concentrations and OH reaction rates

Approaches
-OH loss/reactivity
-Ozone loss/reactivity
-SOA production

Field studies indicate that a large fraction of missing compounds (primary and secondary) indicating we need better analytical techniques
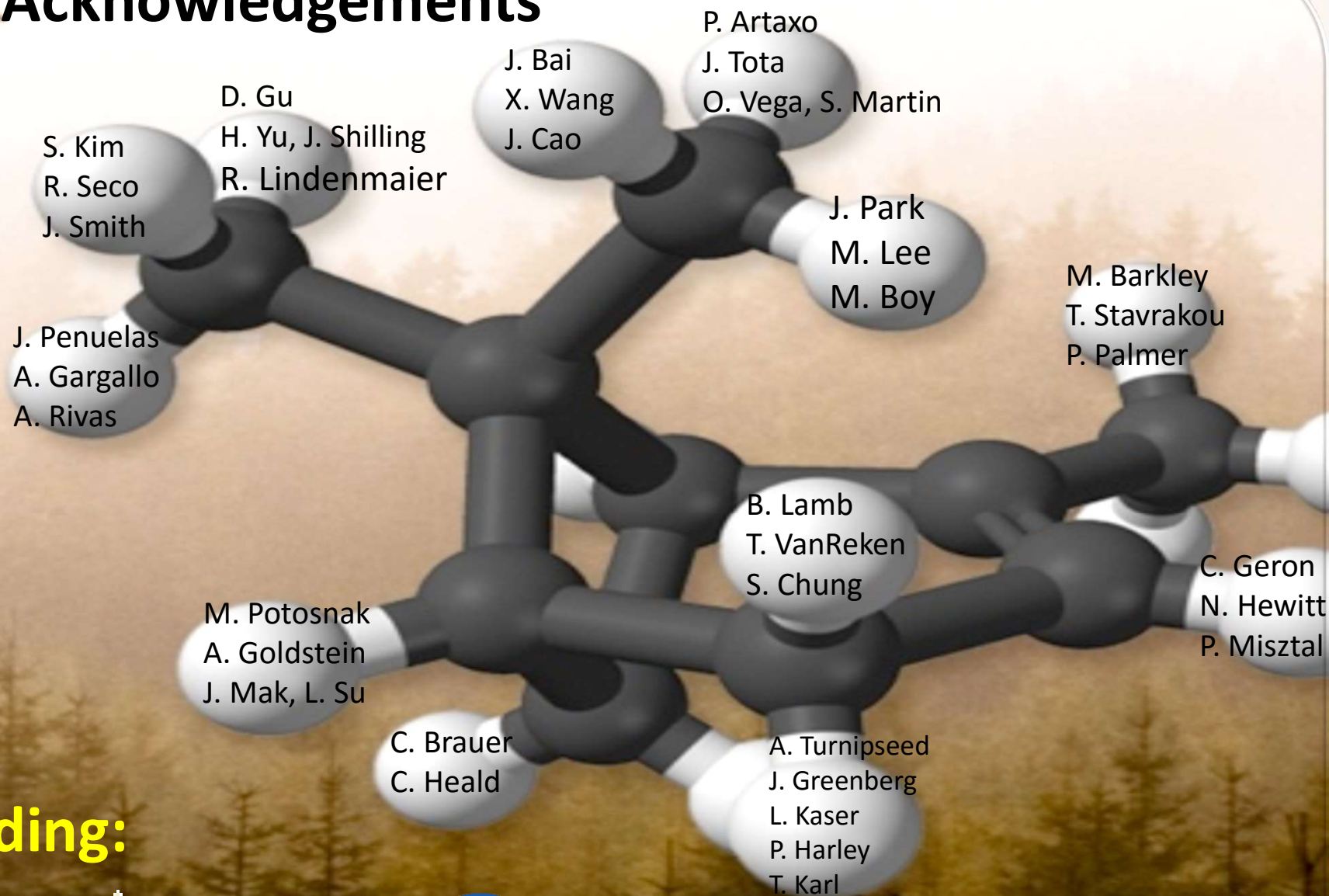
UCI FLUXTRON: Multimodal VOC analysis to identify and quantify the missing compounds
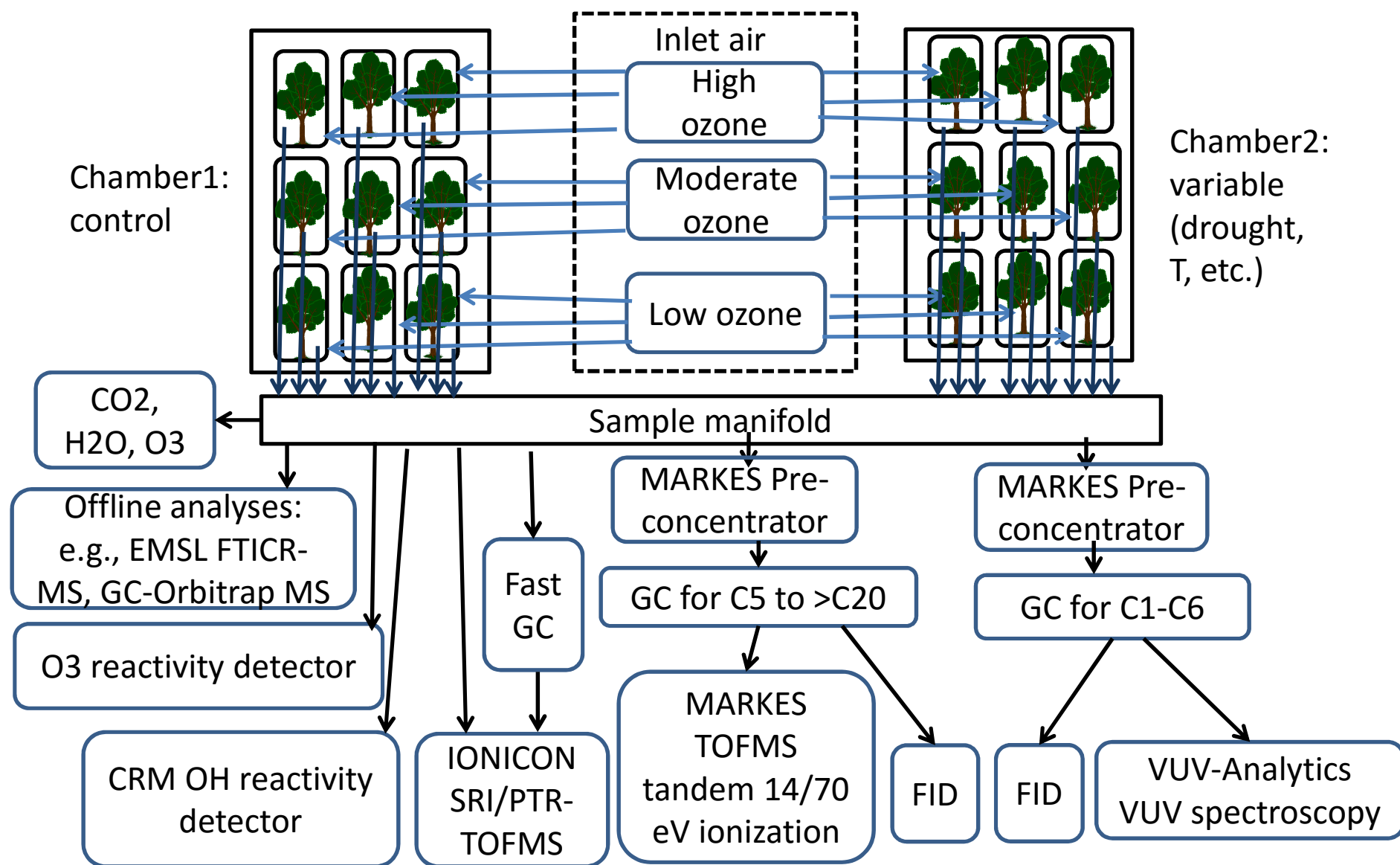
Key Points

- Diverse and abundant plant volatiles influence climate and air quality

- Multi-scale observations enable progress towards modeling emissions and their impacts

- Stress emissions may be important but not well represented and perhaps undetected

- Need better analytical tools to identify and quantify missing compounds

Acknowledgements

S. Kim
R. Seco
J. Smith

D. Gu
H. Yu, J. Shilling
R. Lindenmaier

J. Bai
X. Wang
J. Cao

P. Artaxo
J. Tota
O. Vega, S. Martin

J. Park
M. Lee
M. Boy

M. Barkley
T. Stavrakou
P. Palmer

J. Penuelas
A. Gargallo
A. Rivas

B. Lamb
T. VanReken
S. Chung

C. Geron
N. Hewitt
P. Misztal

M. Potosnak
A. Goldstein
J. Mak, L. Su

C. Brauer
C. Heald

A. Turnipseed
J. Greenberg
L. Kaser
P. Harley
T. Karl

Funding:

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