

# Managing Biogenic VOC to reduce summertime ozone in China

YRD Clean Air Forum

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**BVOC sampling site: YRD 2009**

**Photo: A. Guenther**



# What are Biogenic Volatile Organic Compounds (BVOCs)?

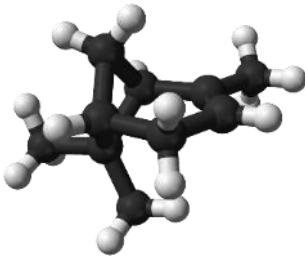
**Biogenic:** produced by living organisms (but can be modified by human activities)

**Volatile:** gas phase (but not all are completely in the gas phase)

**Organic Compounds:** contains C–H covalent bonds (but can include others: O, S, N, Cl ...)



**Pine**



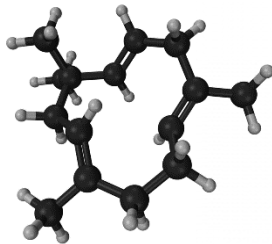
$\alpha$ -pinene



**Anthropogenic**



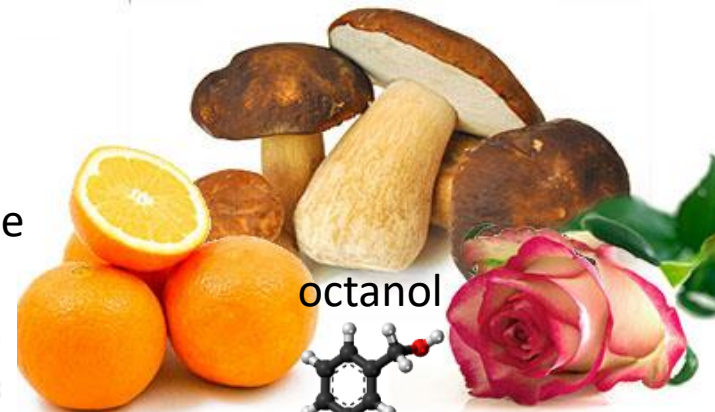
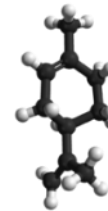
**Hops**



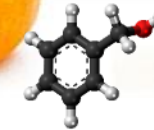
Humulene



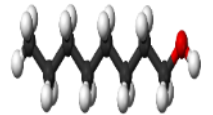
limonene



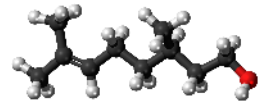
octanol



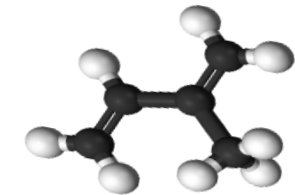
linalool



Citronellol



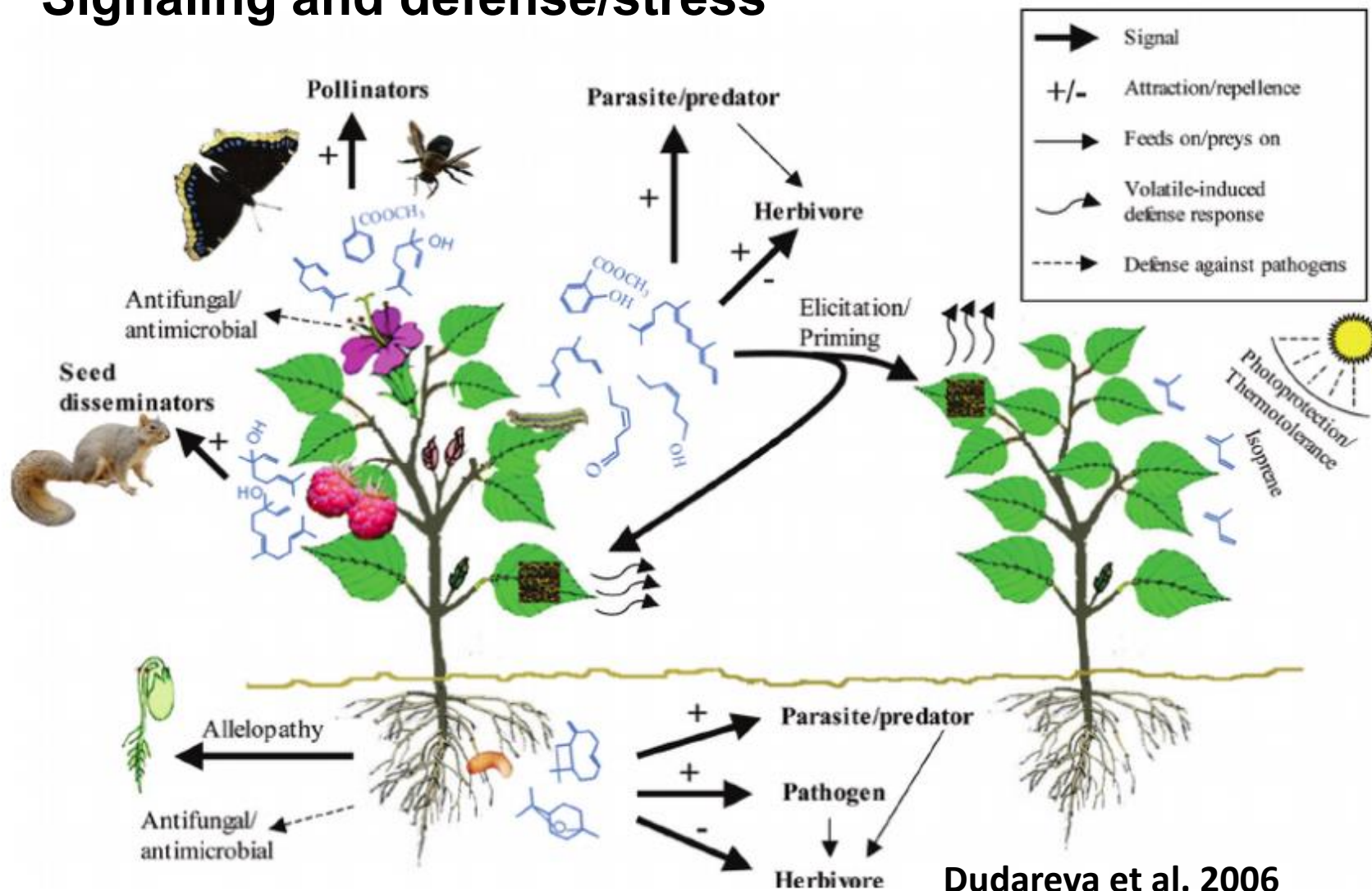
**Oak**



**Isoprene: half of  
global total BVOC**

# Why do organisms emit these Biogenic Volatile Organic Compounds (BVOCs)?

## Signaling and defense/stress

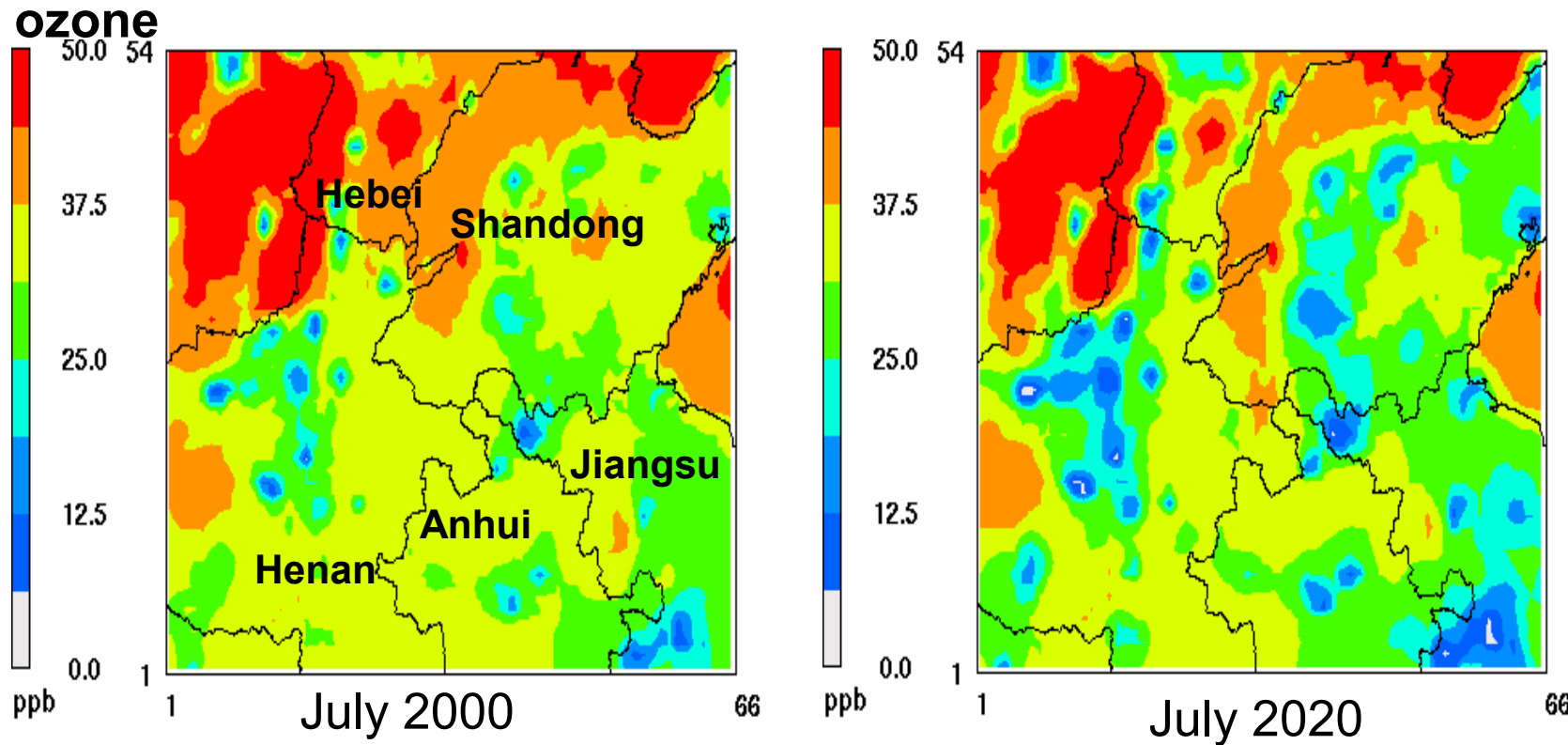


1. Beneficial roles
2. Stress can increase BVOC (but there is a limit)

Dudareva et al. 2006

# “Future” predictions of 2020 ozone concentrations in Central Eastern China

Wang et al. 2005



Anthropogenic and biogenic VOC emissions were both ~4500 kTons

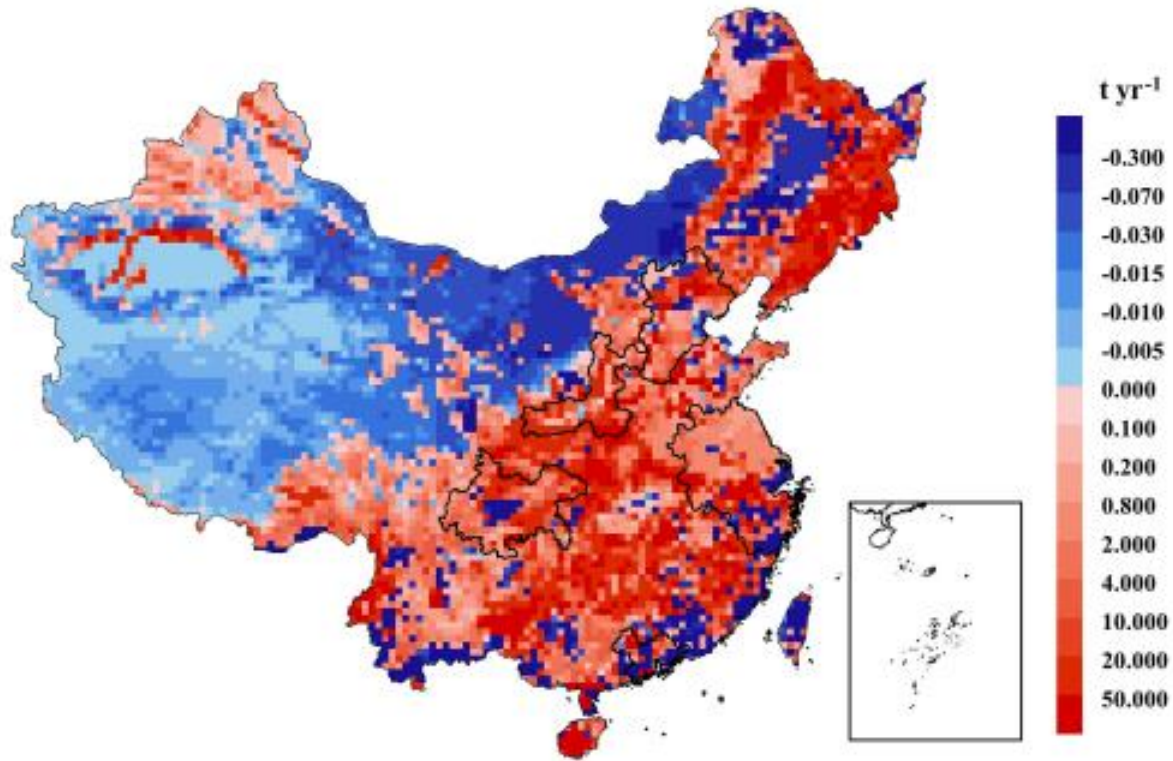
Anthropogenic VOC was assumed to increase by 50% and NO<sub>x</sub> by 150%

A slight decrease in ozone is predicted (associated with increases in NO<sub>x</sub>).

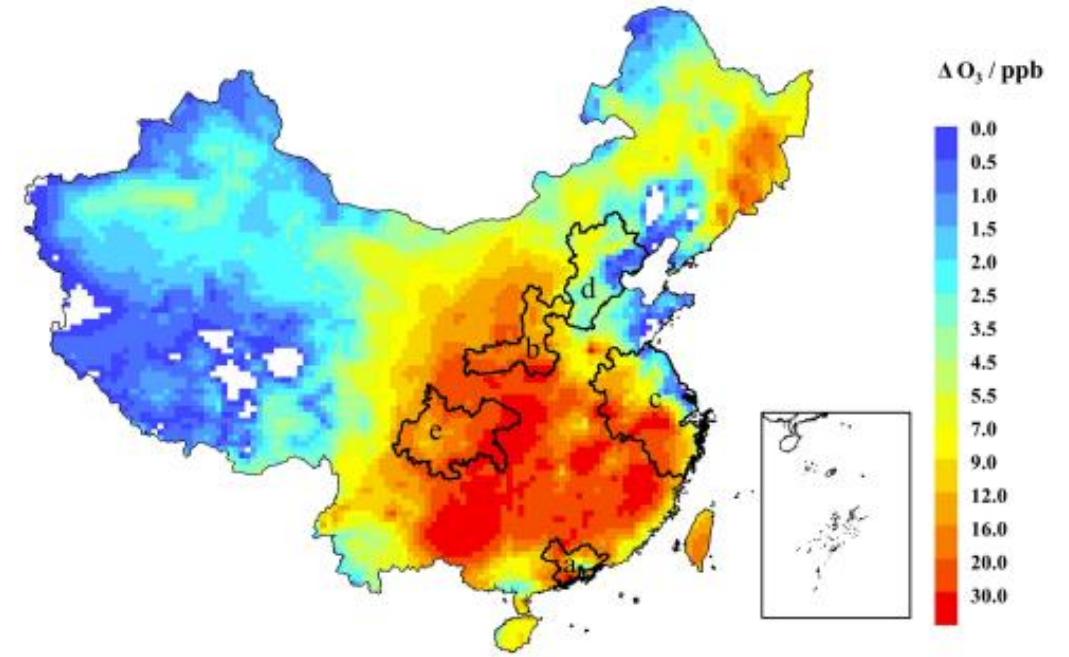
This assumes that biogenic VOC does not change but we noted that is likely that there will be substantial increases in biogenic VOC due to climate and landcover change.



# BVOC emission increase in China during this time period: 1981 to 2018



**Figure 2.** Spatial distribution of interannual variations in BVOC emissions caused by leaf biomass changes.

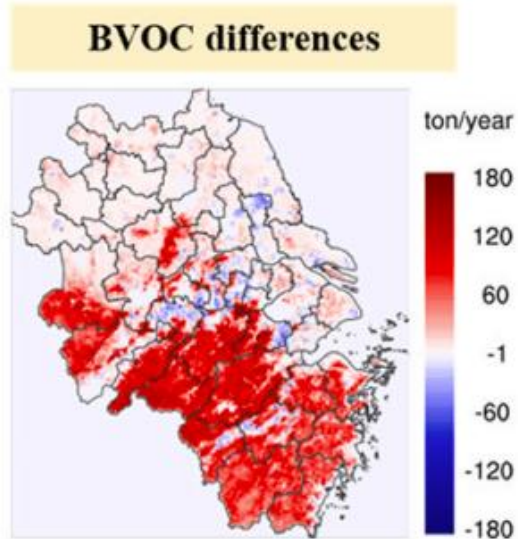


**Figure 3.** Spatial variations in impact of BVOC emission on MDA8  $\text{O}_3$  concentration. The key regions include the (a) Pearl River Delta (PRD), (b) Fenwei Plain (FWP), (c) Yangtze River Delta (YRD), (d) Beijing-Tianjin-Hebei (BTH), and (e) Chengdu-Chongqing (CC).

**BVOC impact on MDA8 ozone is up to  
20 to 30 ppb- including in eastern YRD**

**Cao et al. 2022**

# Sensitivity of YRD ozone mitigation strategies to BVOC emission estimates



Absolute ( $\mu\text{g}/\text{m}^3$ ) and relative contribution (%) of MDA8 from different BVOC emissions for selected cities in the YRD region during June 2021.

City	$\Delta\text{MDA8}$ ( $\mu\text{g}/\text{m}^3$ ) due to BVOC emissions		Relative contribution (%)	
	MODIS	ESA	MODIS	ESA
Hefei	13.8	18.8	8.8%	11.5%
Nanjing	10.7	15.0	6.9%	9.5%
Hangzhou	11.1	14.0	8.0%	9.8%
Shanghai	3.1	4.7	2.7%	4.1%

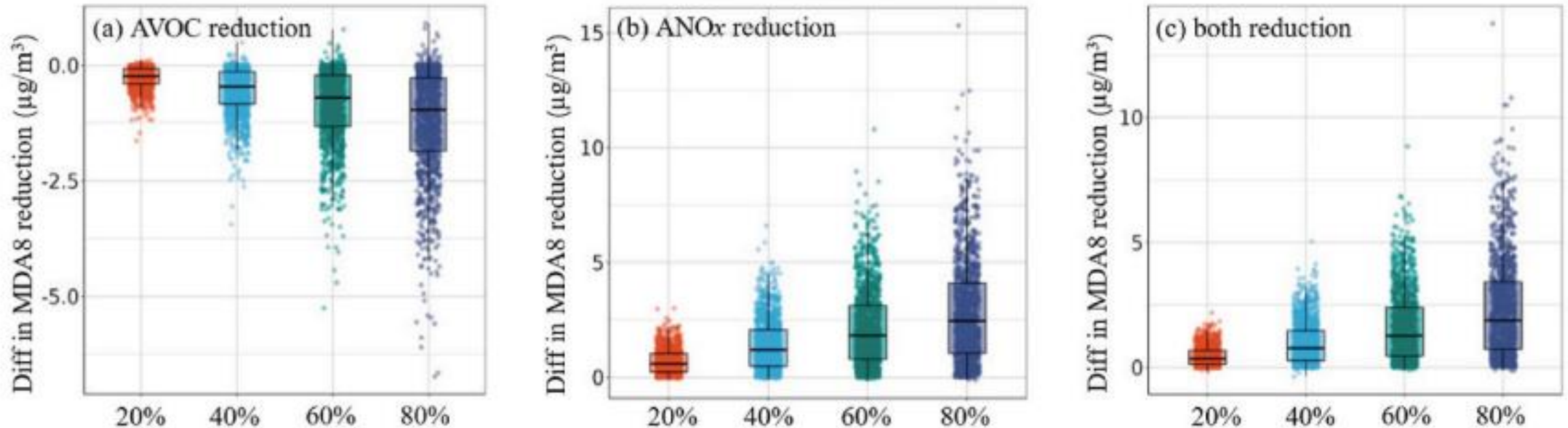
Huang et al. 2024

MDA8 ozone concentrations

Uncertainties in BVOC emission estimates impact ozone predictions

# Sensitivity of YRD ozone mitigation strategies to BVOC emission estimates

Huang et al. 2024

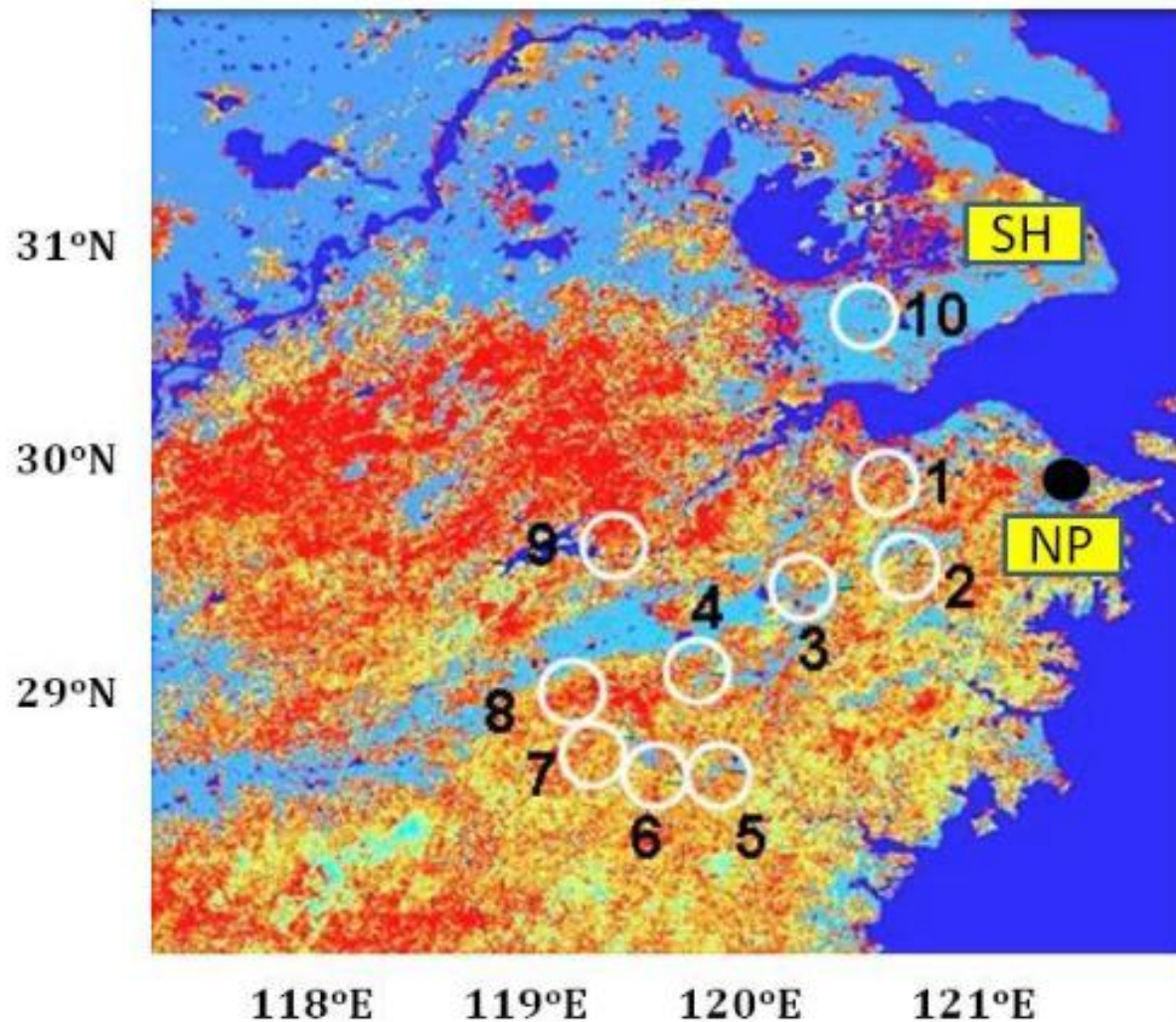


Differences in the city-level daily MDA8 (ESA – MODIS, unit:  $\mu\text{g}/\text{m}^3$ ) in response to different emission reduction scenarios in the YRD. The x-axis represents different reduction ratios.

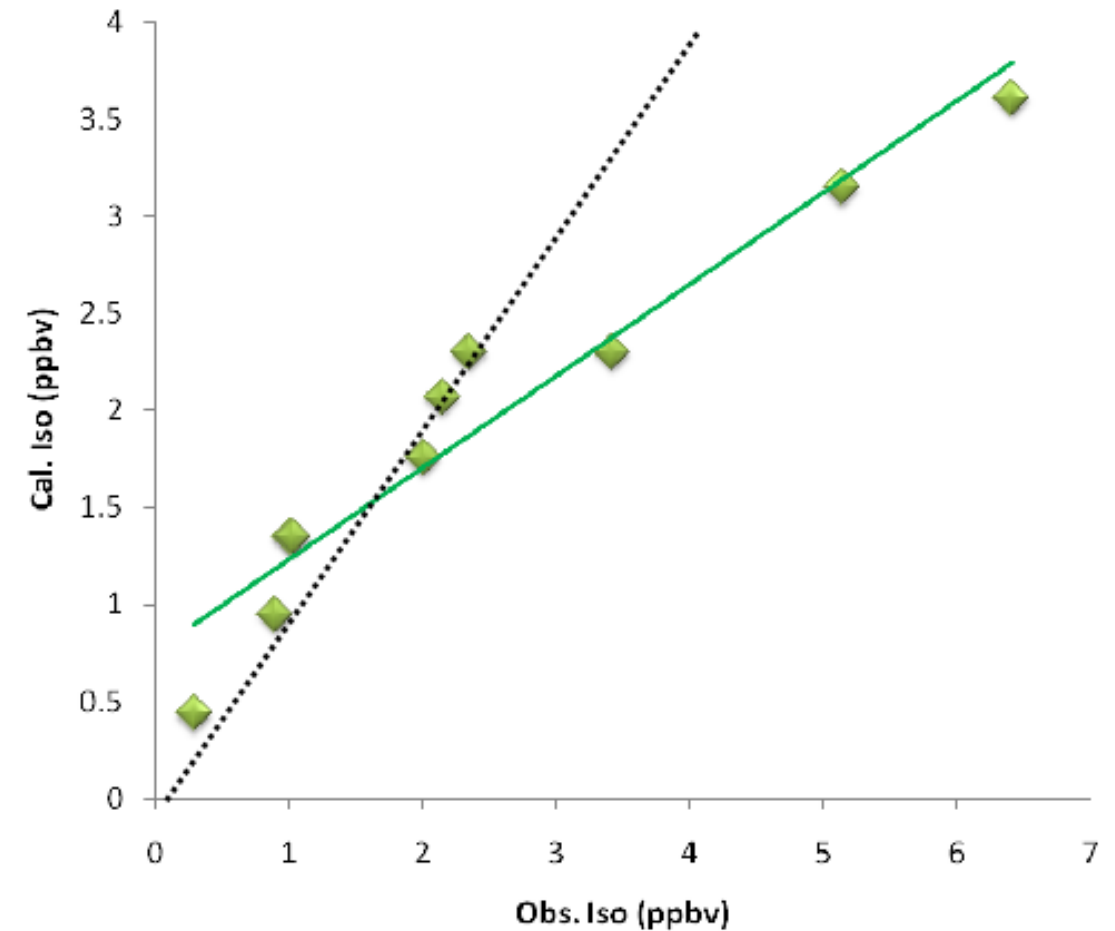
**BVOC can influence ozone control strategies (NOx vs AVOC control)**



# Effect of forest isoprene emissions on ozone formation in Shanghai



**Fig. 1.** MEGAN isoprene emission rates and measurement locations in the forests south of Shanghai.



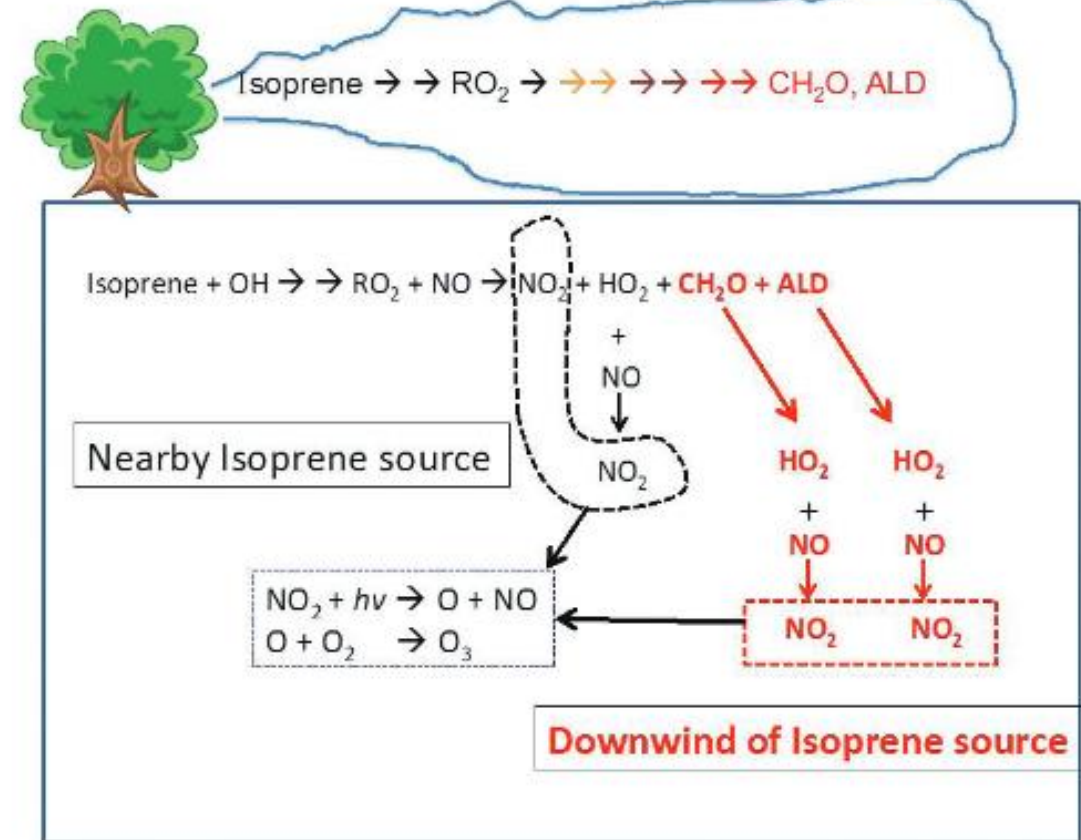
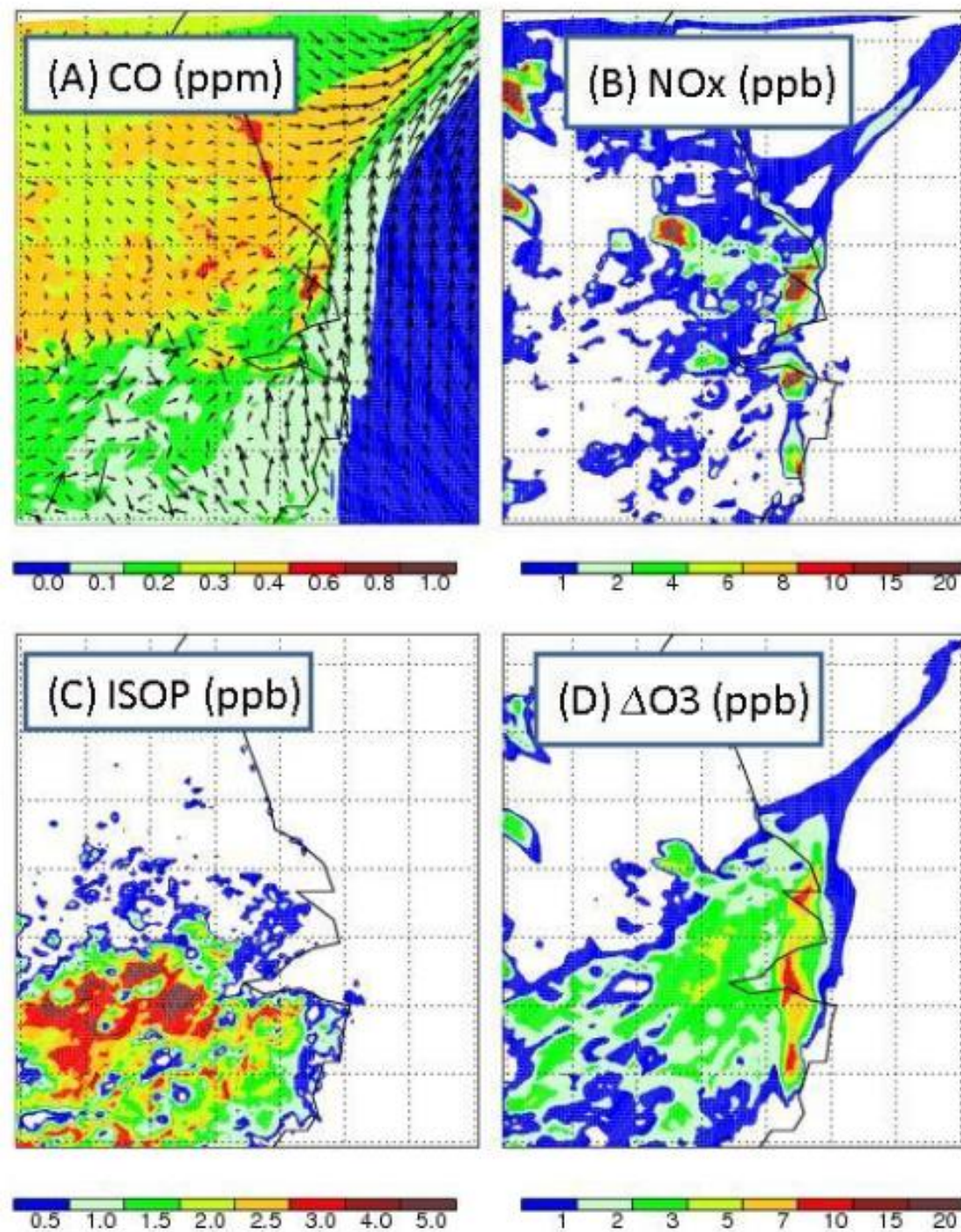
**Fig. 3.** One by one comparison of the calculated and measured isoprene concentrations. The green line is the fitting line of all the points, and the black dot line is the 1:1 line between the calculations and the measurements.

**Geng et al. 2011**



## July 12 2009 case study

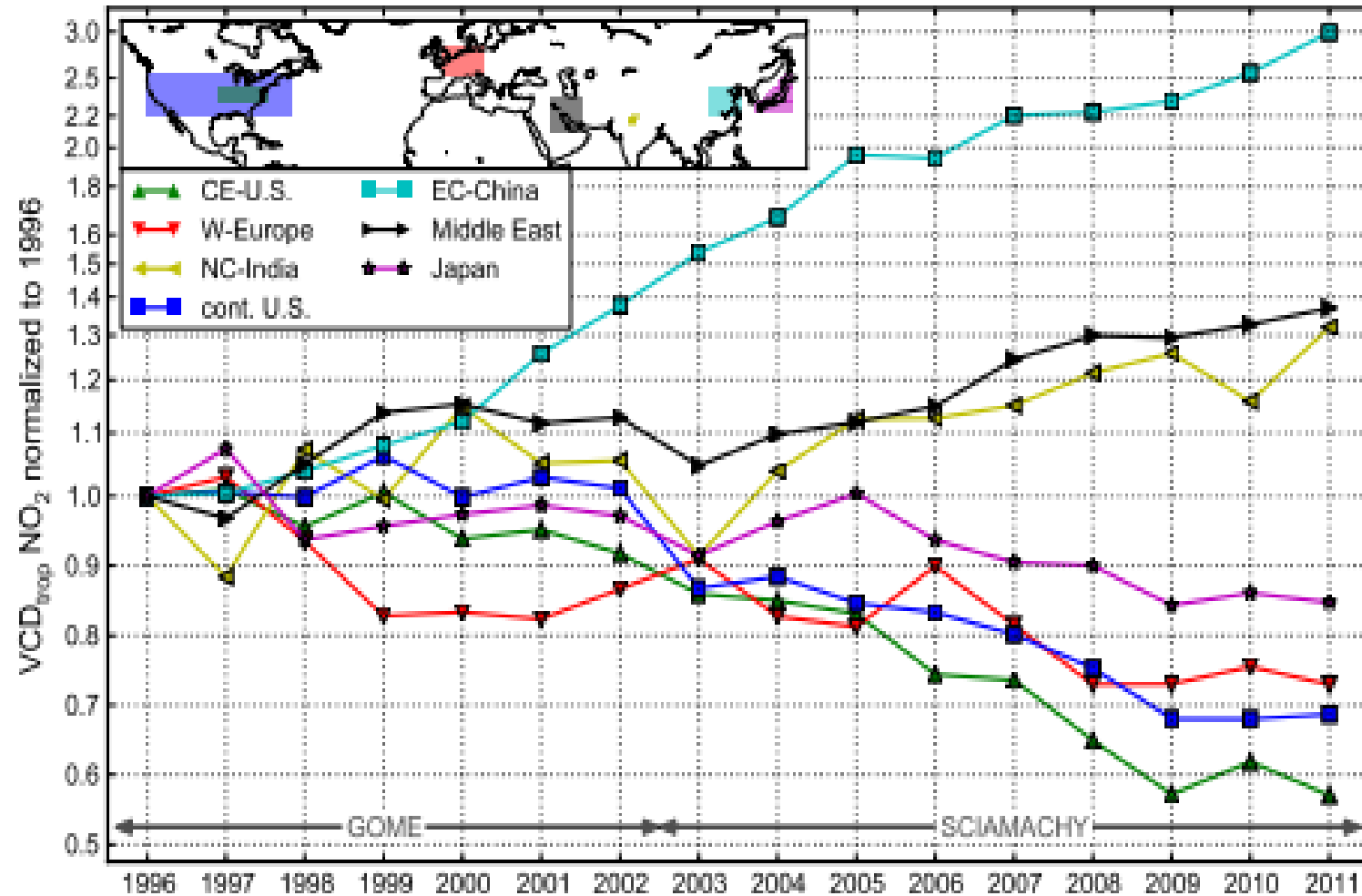
10 ppb increase in ozone when forest isoprene source is included in WRF-chem



**Fig. 7.** Schematic picture illustrating the impact of biogenic emissions on the photochemical production of ozone in the forest source area and urban areas downwind of the forests.

**Geng et al. 2011**

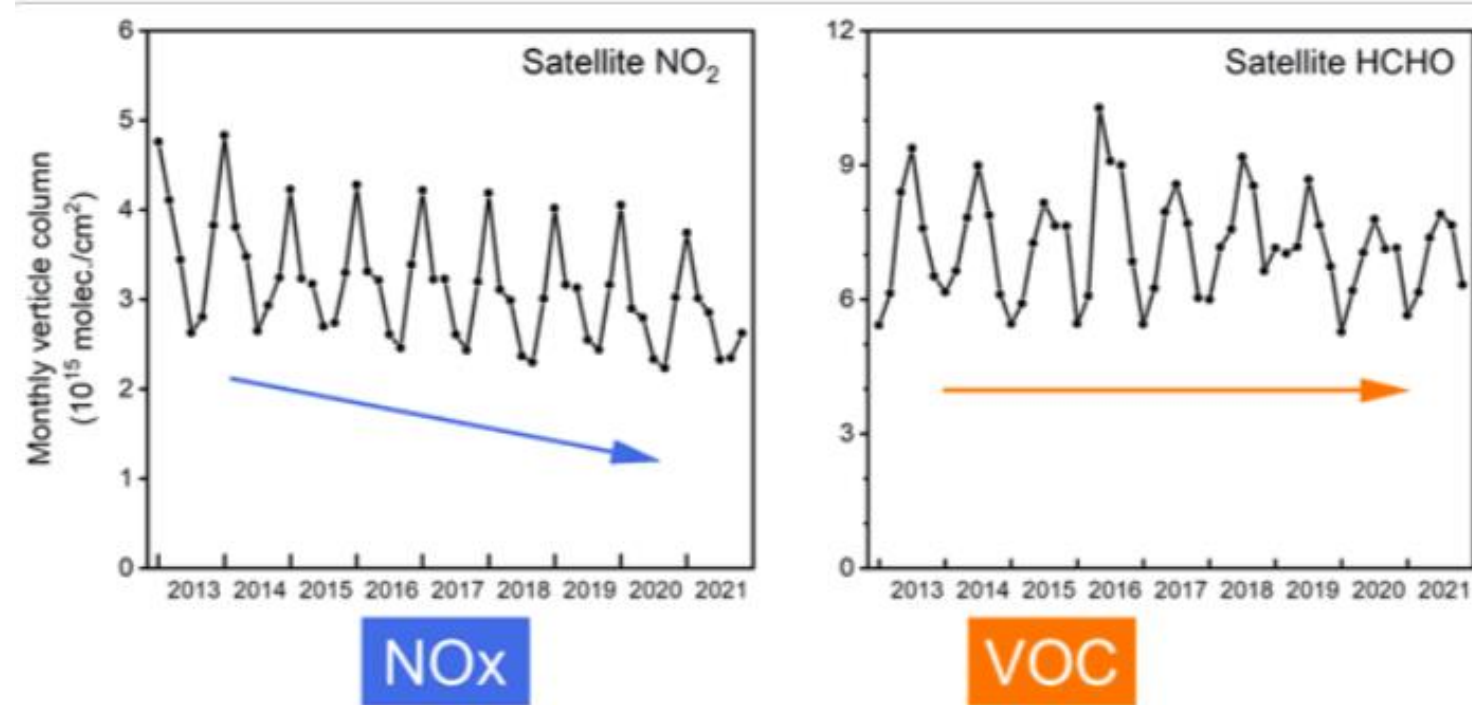
## 2000 to 2011: NO<sub>2</sub> rapidly increased in China and decreased in US



Satellite estimates of NO<sub>2</sub> trends

Hilboll et al. 2012

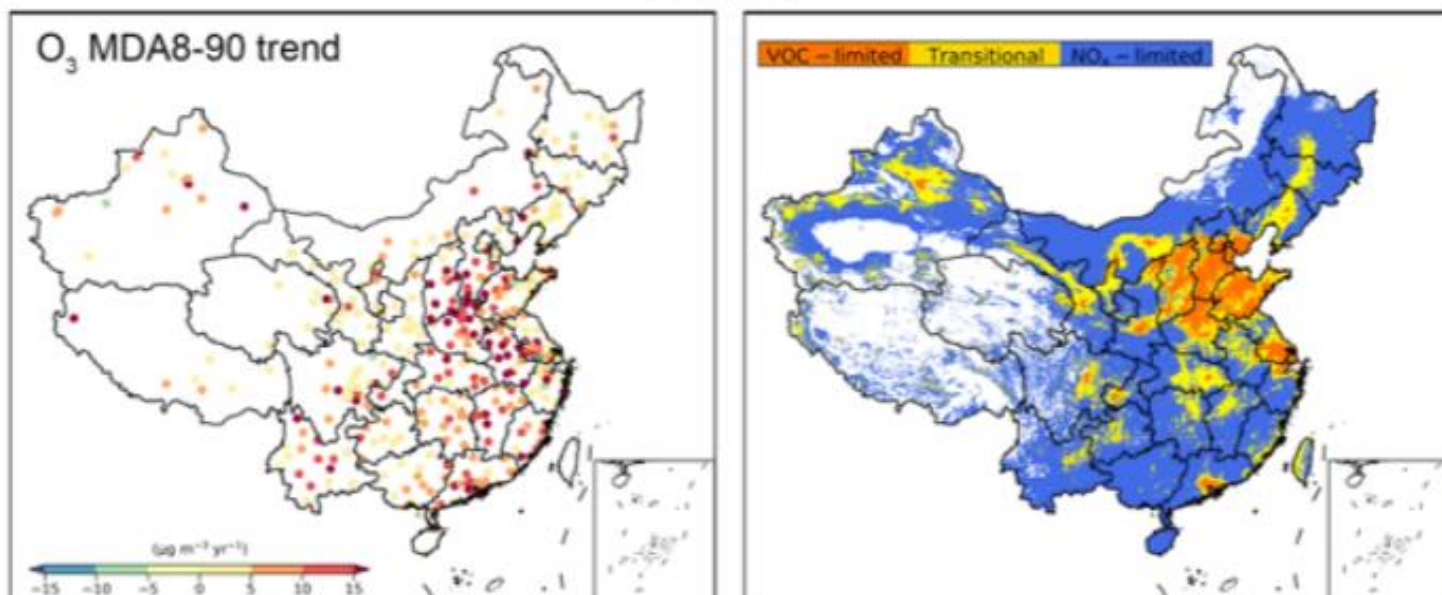




**NO<sub>2</sub> is starting to decrease in China but VOC is not**

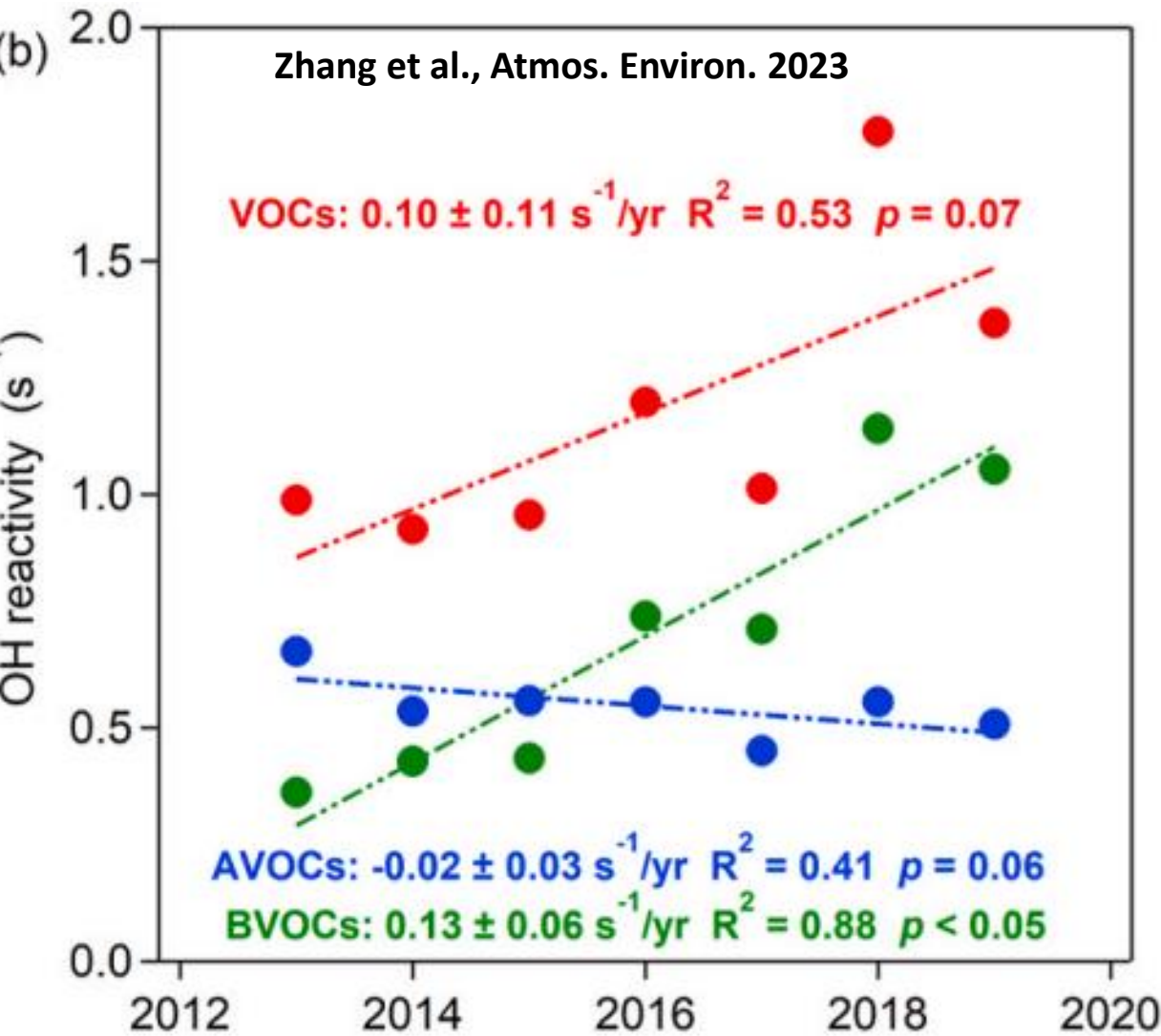
**Anthropogenic VOC may be decreasing but is balanced by increasing biogenic VOC**

Ren et al. 2022

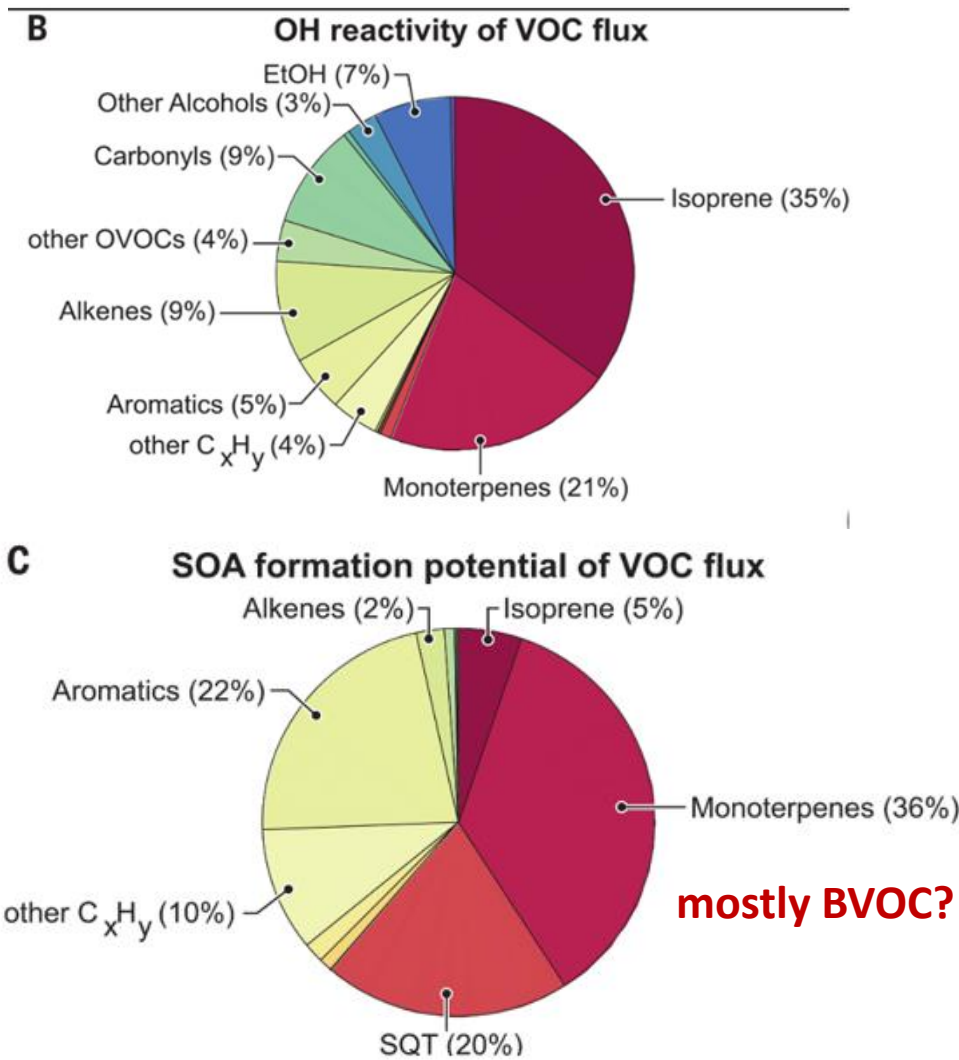


# Biogenic VOC is dominating over anthropogenic VOC even in urban areas

Hong Kong VOC OH reactivity dominated by BVOC



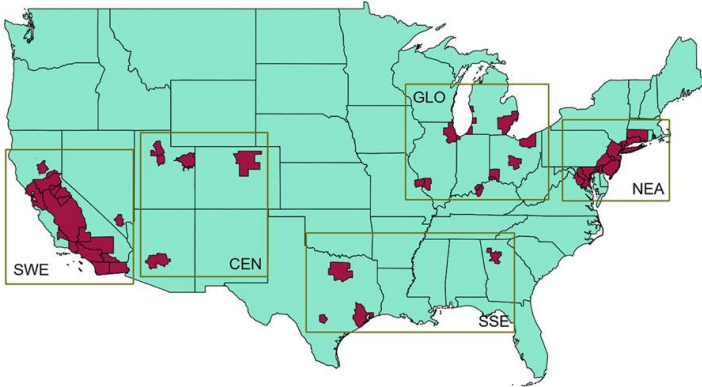
Los Angeles VOC OH reactivity and SOA formation potential dominated by BVOC



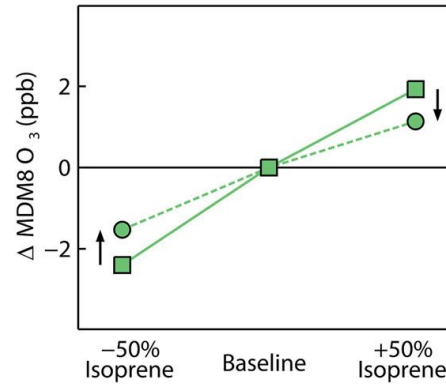
RECAP aircraft flux study (Pfannerstill et al. 2023, 2024)



(a) Nonattainment Areas (Pop = 133.1 Million)



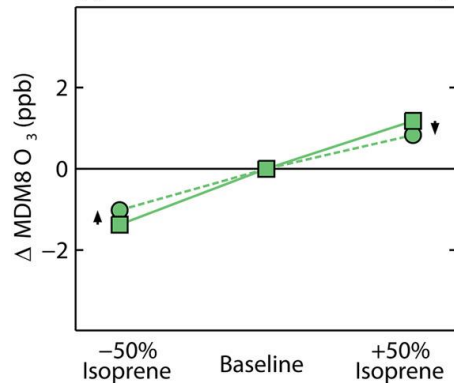
(b) Southwest Nonattainment Areas (Pop = 39.6 Million)



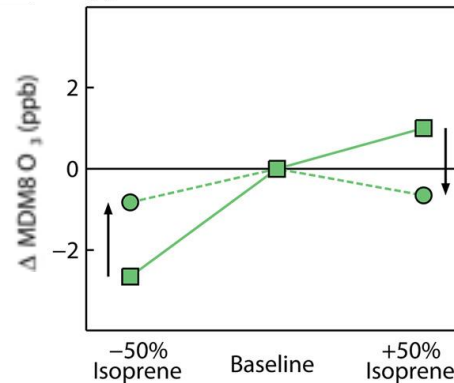
Following anthropogenic NO<sub>x</sub> reductions, O<sub>3</sub> sensitivity to biogenic VOC decreased in many O<sub>3</sub>-nonattainment areas.

Soil NO<sub>x</sub> is becoming the most important biogenic emission in rural areas

(c) Central Nonattainment Areas (Pop = 10.6 Million)

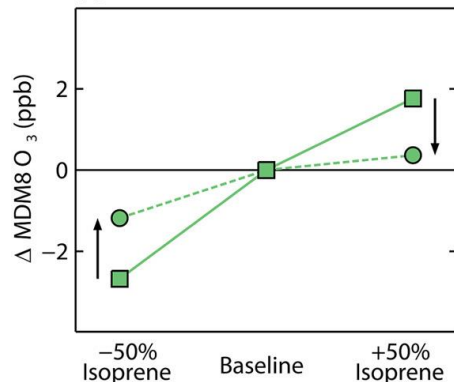


(d) South and Southeast Nonattainment Areas (Pop = 19.7 Million)

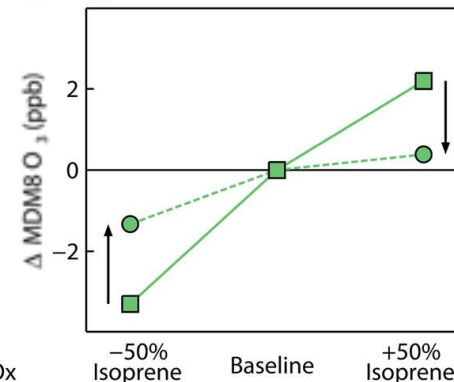


Maximum daily 8-hour average ozone response to BVOC in 2006 compared to 2017

(e) Great Lakes and Ohio River Nonattainment Areas (Pop = 24.3 Million)



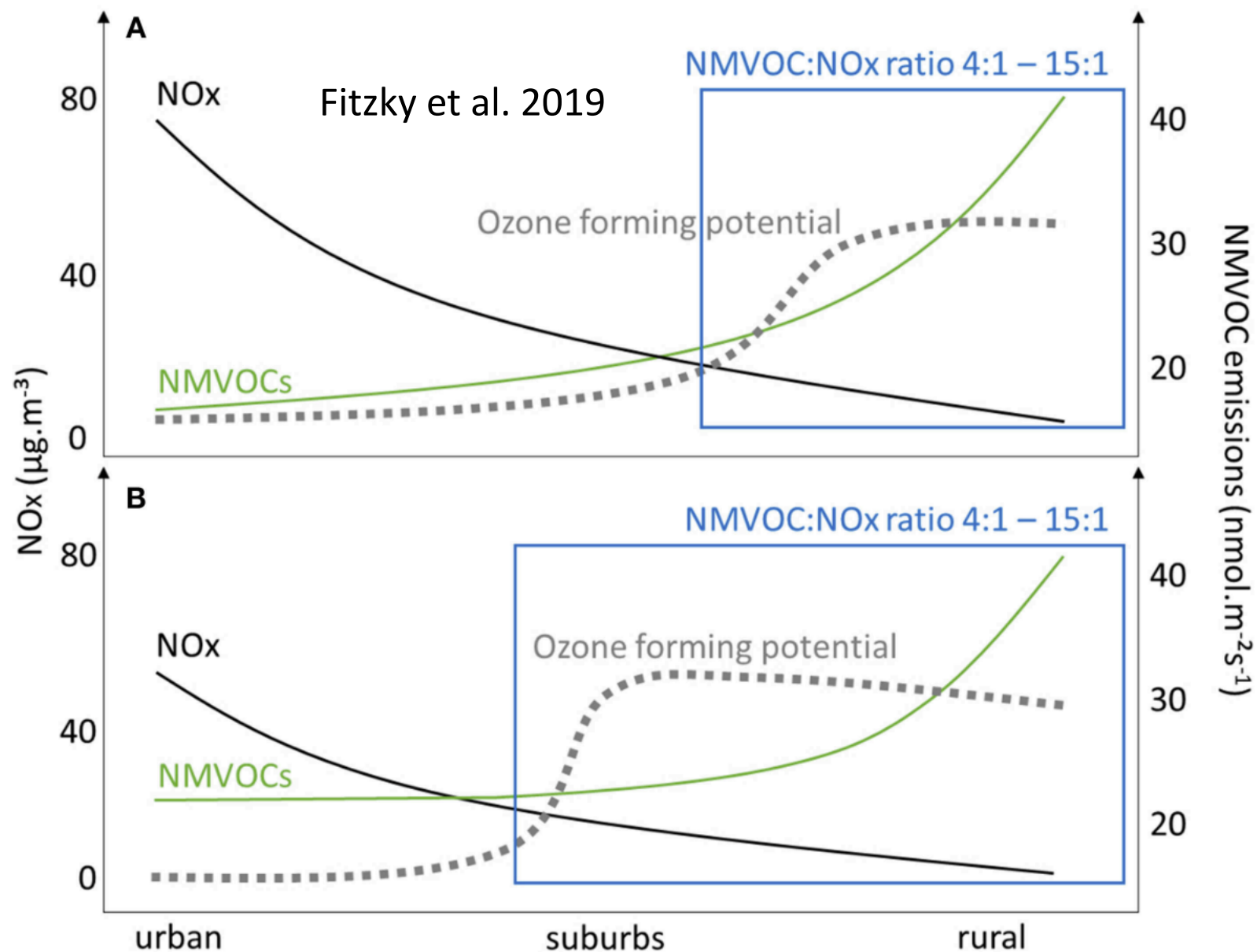
(f) Northeast Nonattainment Areas (Pop = 38.9 Million)



Solid lines (squares): sensitivity for 2006 anthropogenic NO<sub>x</sub>

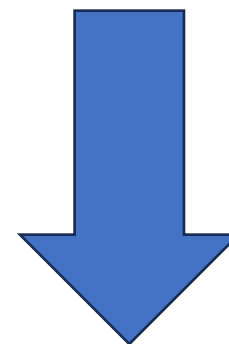
Dashed lines (circles): sensitivity for 2017 anthropogenic NO<sub>x</sub>

# Main BVOC impacts are shifting from rural to urban



Suburban and even urban areas are changing from

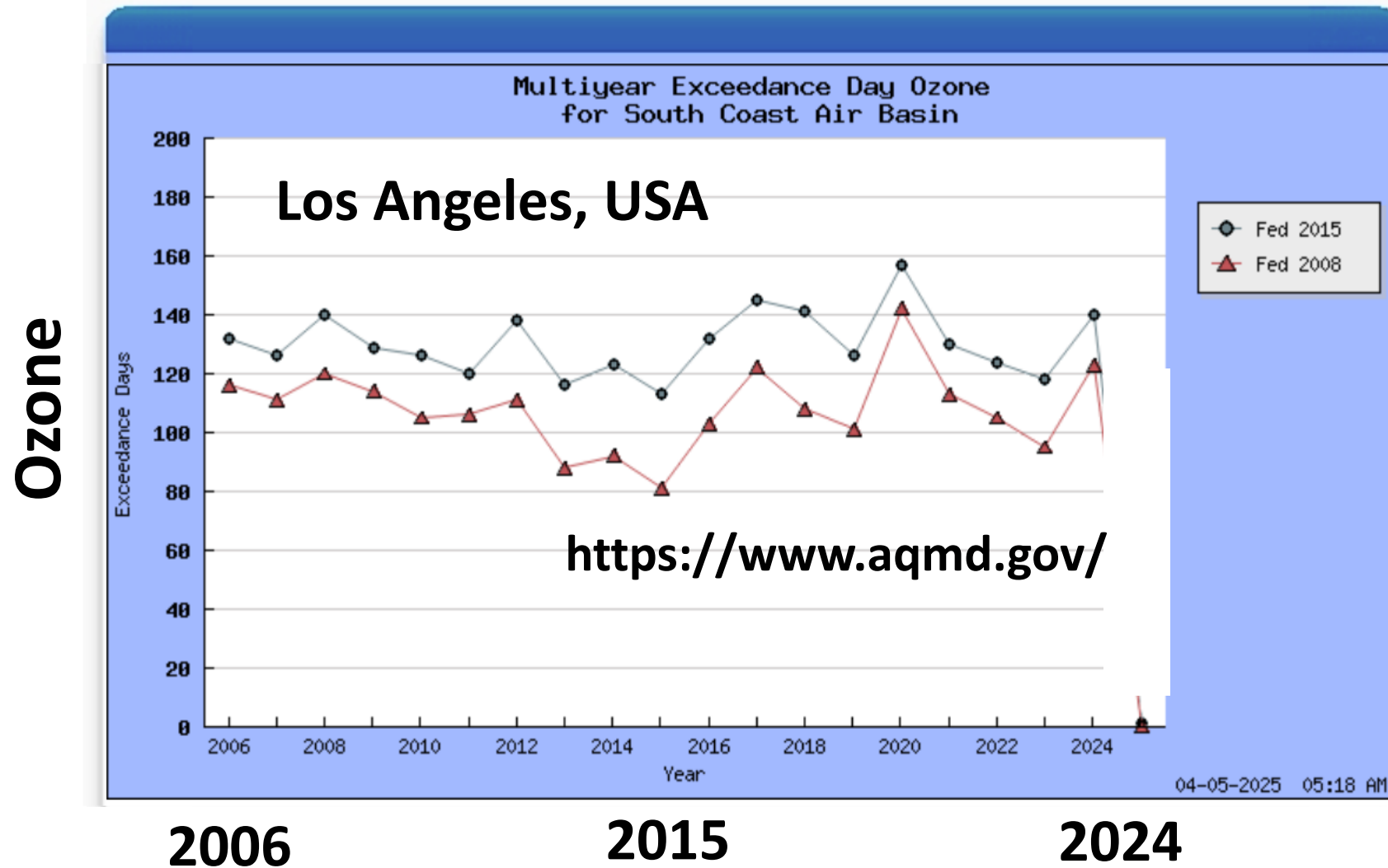
High NO<sub>x</sub>  
Low BVOC



Decreased NO<sub>x</sub>  
Increase BVOC



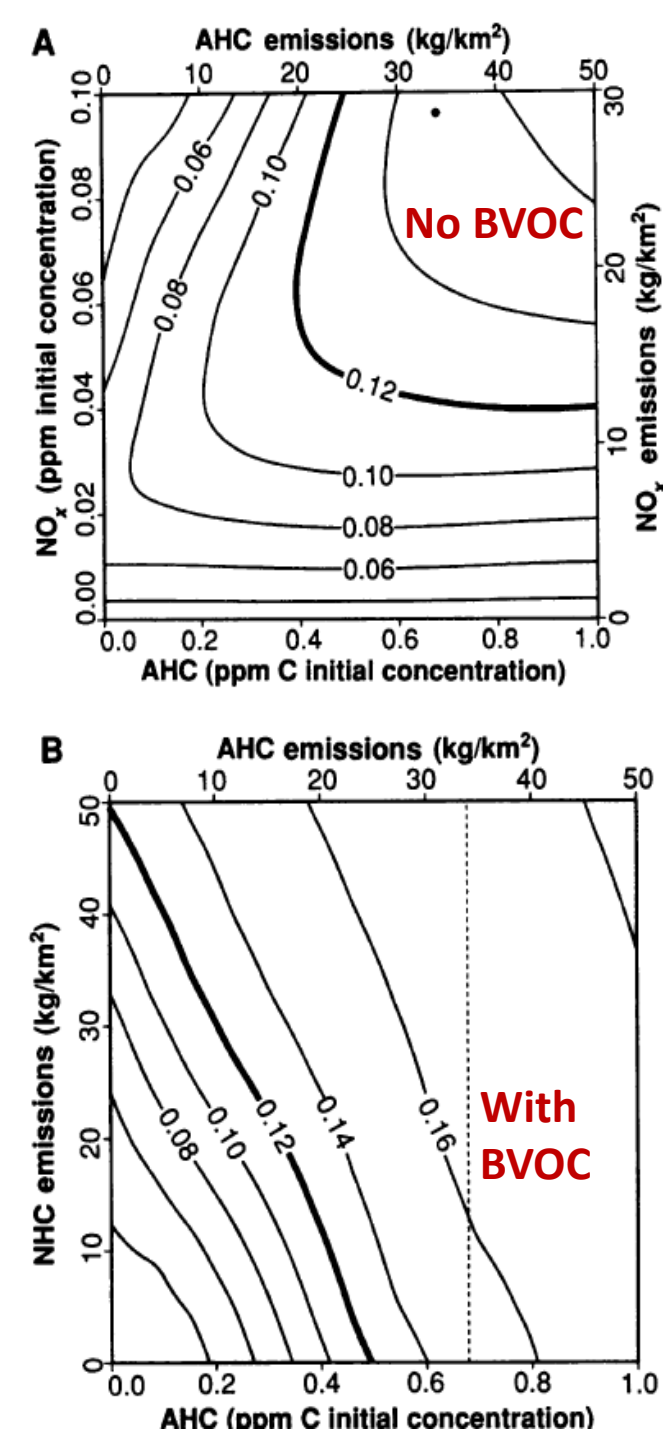
# Persistent ozone concentrations in urban LA even with decreasing anthropogenic VOC and NO<sub>x</sub>



# BVOC impacts on ozone

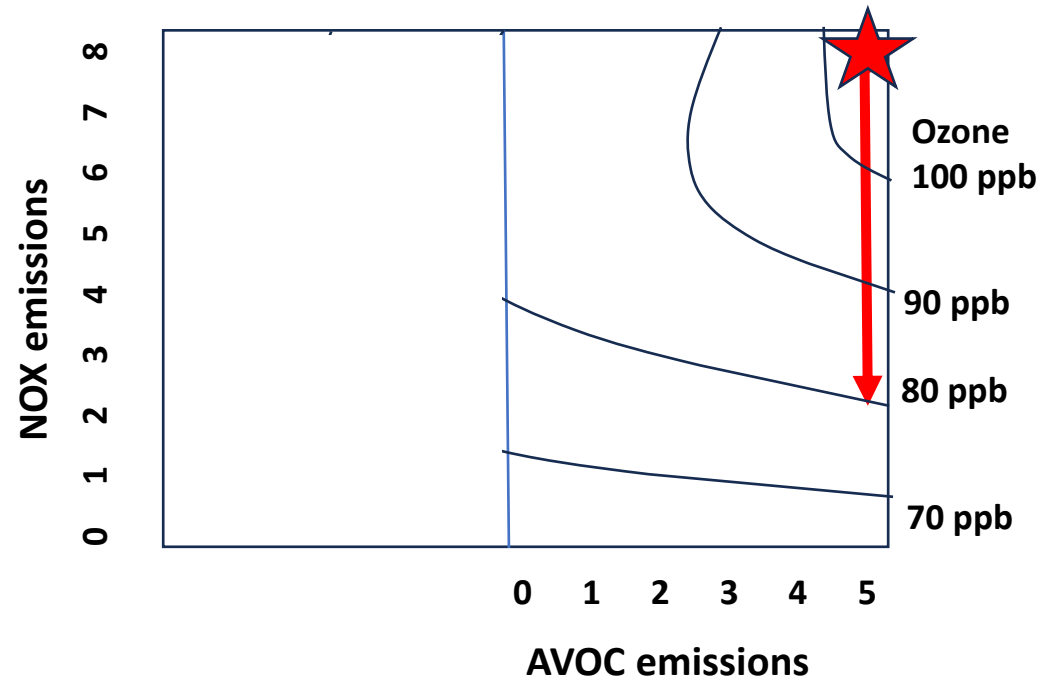
## Chameides et al 1988

- BVOC can contribute to ozone production
- Reducing anthropogenic VOC looks like the best ozone abatement strategy but not when you include BVOC
- Conclusion: decrease NO<sub>x</sub> emissions to reduce ozone

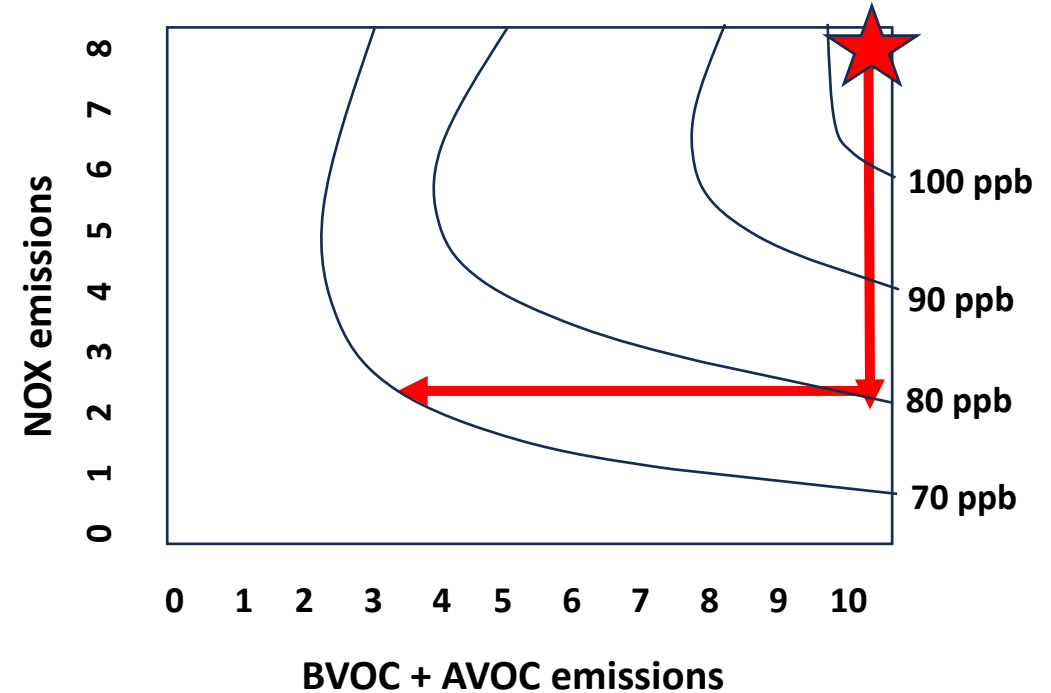




# How can we get Los Angeles ozone to the level recommended by WHO (and required by USEPA)?



**NOx emission reductions  
may work only so far**



**May need to consider BVOC emissions  
to achieve lower ozone levels**

# MEGAN BVOC Emission Rate Estimates

$$\text{Emission Rate} = S \times EF \times EA$$

Emission Rate: Emission to atmosphere

Guenther et al. 2012

Source Density: Amount of source per land surface area

Emission Factor (EF): Emission rate at “standard” conditions. It is dependent on the amount and type of biogenic sources in a landscape.

Emission Activity (EA): Nondimensional factors that account for all emission variations (equal to unity at standard conditions). Dependent on environmental conditions including meteorology, atmospheric composition, landcover... (anything that causes emissions to vary)

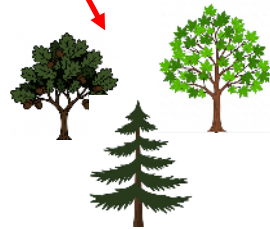
$$\text{Emission} = LAI \cdot \epsilon \cdot \gamma_T \cdot \gamma_P \cdot \gamma_A \cdot \gamma_{CO_2} \cdot \gamma_{SM}$$

**LAI (Leaf Area Index):**  
Source density

**$\epsilon$ : Emission factor**



Landscape capacity to emit BVOC



Activity dependent change  
in BVOC emission

- $\gamma_T$  = Temperature
- $\gamma_P$  = Psyn Active Radiation
- $\gamma_A$  = Leaf age
- $\gamma_{CO_2}$  = CO<sub>2</sub> concentration
- $\gamma_{SM}$  = Drought, other stress

# How can urban BVOC emissions be controlled?

**Do we know which plants are the low BVOC emitters?**

## Emission control strategies

- Manage stress: stressed plants emit more BVOC
- Manage maintenance: harvesting, pruning and mowing are a source of BVOC wound compounds
- **Manage plant selection (high vs low emitters differ by more than 1000x)**

## Implementation approaches

- Increase awareness: Need a simple index
- Cost (Tax, fees, cap and trade)
- Bans (or limits) of targeted tree species





# How do we know which trees to select?

## Issue #1: Emissions data are unavailable or inaccurate



### SelectTree

A TREE SELECTION GUIDE

Enter a tree name...



RESOURCES ▾

DETAILS ▾

LOGIN



SEARCH PACIFIC  
ISLANDS



SEARCH  
CHARACTERISTICS



SEARCH TREE LISTS



APPRAISALS

### SEARCH BY CHARACTERISTICS

### MAIDENHAIR TREE

*Ginkgo biloba*

FAMILY Ginkgoaceae

See: all *Ginkgo* or *Champion*



### CONSIDERATIONS

Branch strength: Strong

Root damage potential: Moderate

Potential health issues: Allergy, Irritant

Biogenic emissions: Moderate

Wildlife interactions: Attracts squirrels

Disease and pest susceptibility: Anthracnose

Disease and pest resistance: Armillaria, Root Rot

Utility friendly: No

WCISA Appraisal: Suggested LCANT 24" box, Suggested LCANT 24" box, Group Rating 2, Approx. cross sectional area 2.24 sq. in.

[selecttree.calpoly.edu](https://selecttree.calpoly.edu)

1. Need an index that indicates the importance of this trait (e.g., Potential Air Pollution Index)
2. Need updated database. For example, Ginkgo is a very low emitter

# How do we know which trees to select?

## Issue #2:

Light dependent (not stored) emissions (**isoprene**, MBO, monoterpenes) can be suppressed or elevated by past environmental conditions

Plant stress or environmental conditions (i.e. sufficient light growth environment?) unknown for most reported data

Assuming all broadleaf isoprene emitting trees have a similar isoprene emission may be reasonable for regional to global modeling but is not sufficient for tree selection

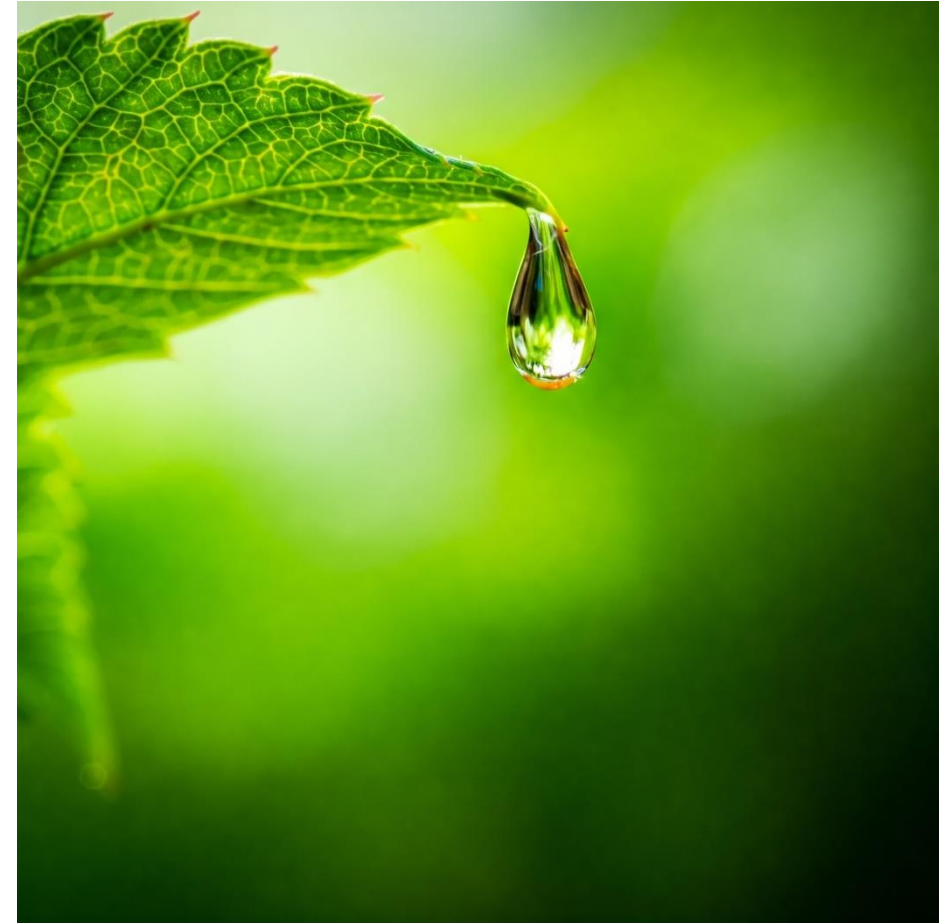


# How do we know which trees to select?

## Issue #3:

**Plants with BVOC storage structures have high variability and can be disturbed by enclosure measurements**

- Enclosure systems are known to damage storage structures causing artificially increased emission rates. This has led to omission of high “outliers”.
- It appears that there are “super-emitters” in the real-world that significantly contribute to total BVOC emissions.
- Need new emission factors survey methods to characterize representative emissions (including super-emitters) for tree selection purposes



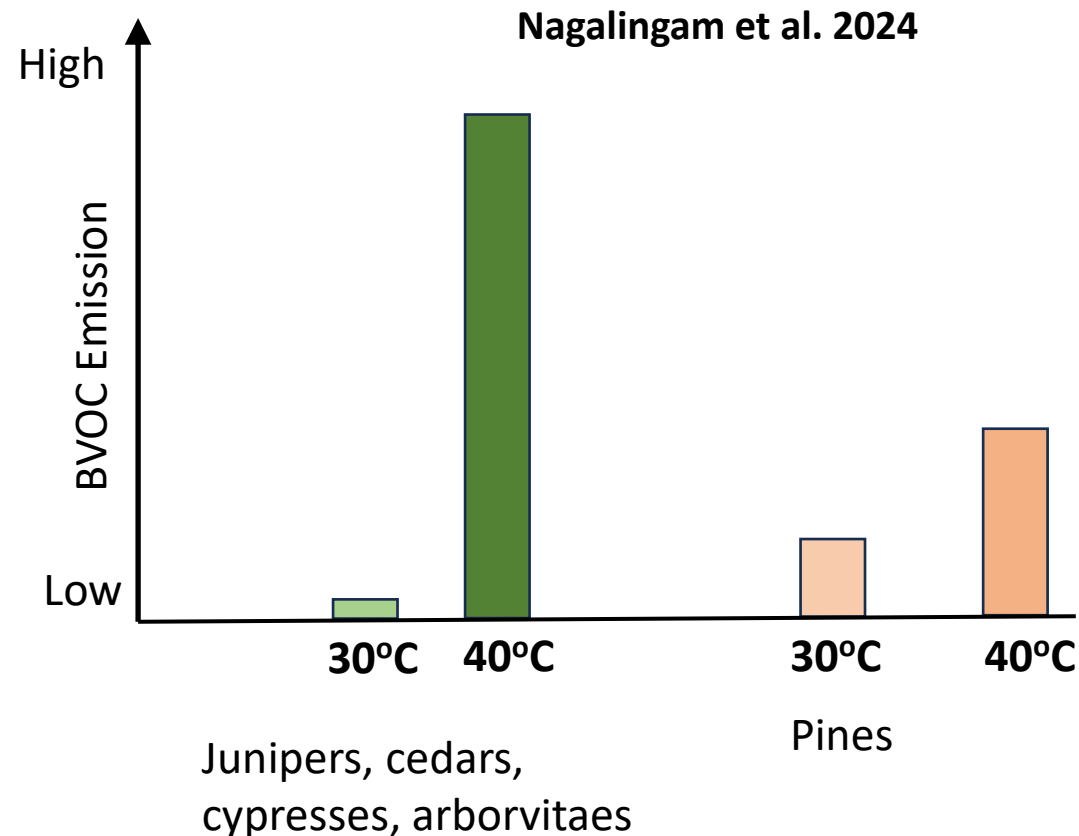


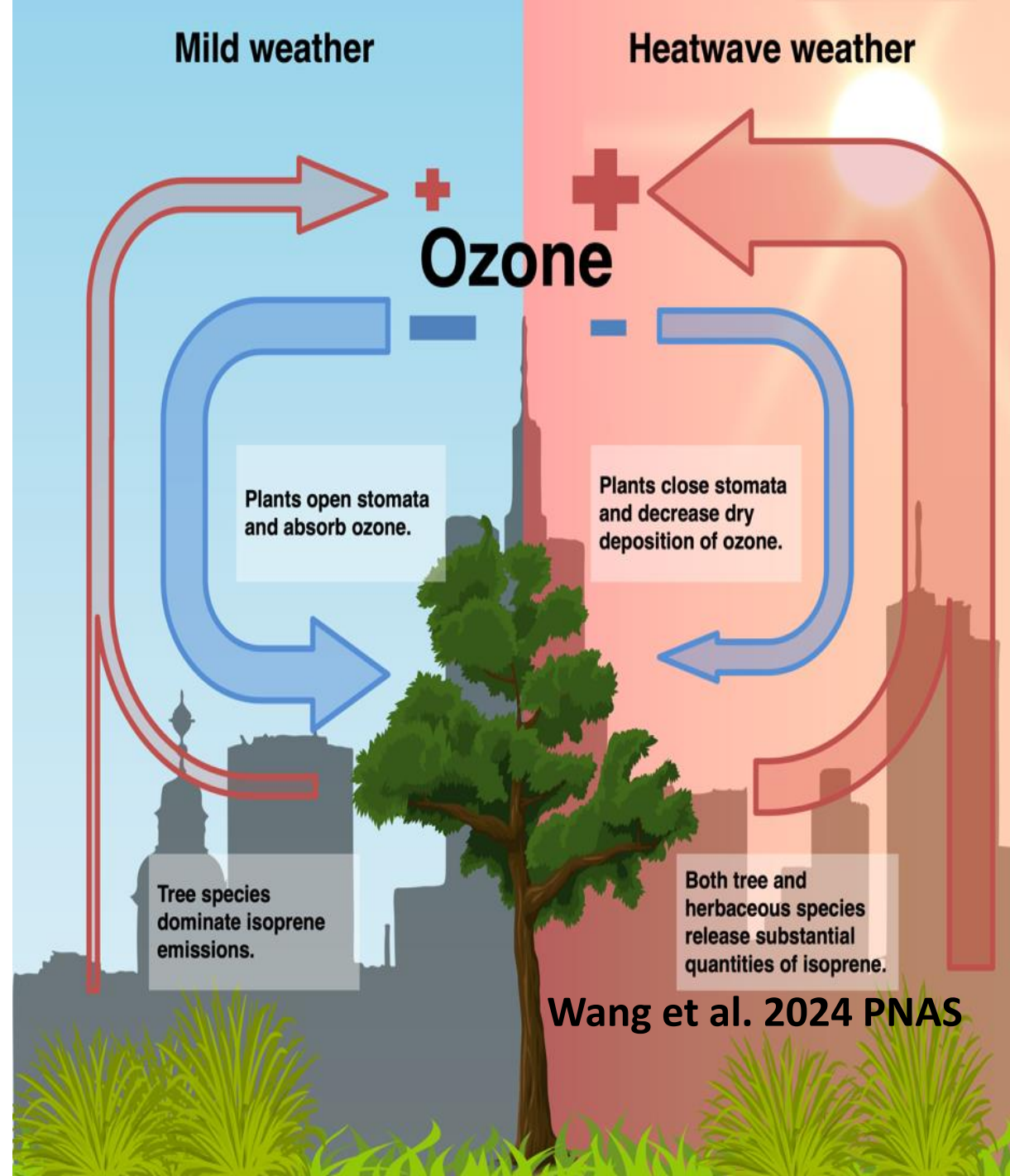
# How do we know which trees to select?

Issue #4:

## Stress induced emission potential

- Some plants are low emitters under optimal conditions but high emitters under stress conditions
- Stress conditions (e.g., heat waves) can be associated with poor air quality events
- Need new emission factor survey methods to identify stress-sensitive species for tree selection purposes

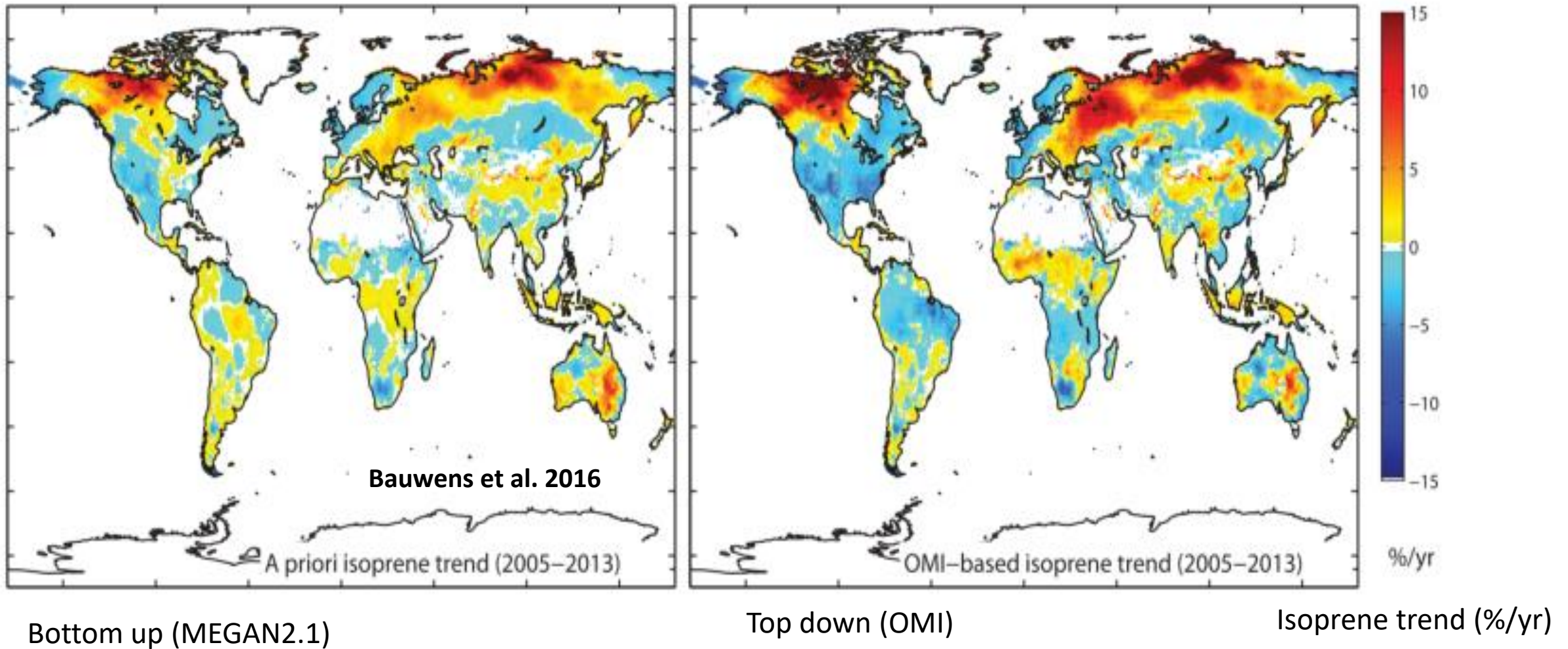




**We may be missing some important plant species altogether**

**Sedges (grass-like plants) are not included in BVOC emission inventories but may be a major source of isoprene during heatwaves**

## How can we assess/monitor/validate BVOC emission estimates?

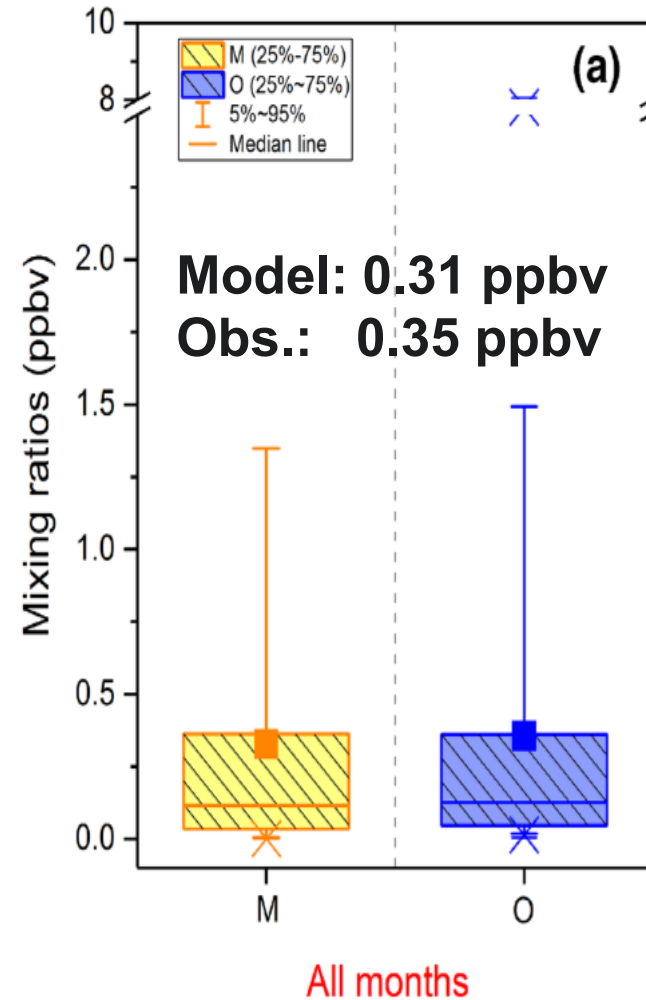


**New satellites (geostationary, multi-compound, high spatial resolution) and calibration efforts may improve these data**



# How can we assess/monitor BVOC emission estimates?

1731 surface layer isoprene measurements at 20 sites in China



Zhang et al. 2020

North

Model: 0.14 ppbv  
Obs.: 0.37 ppbv

South

Model: 0.53 ppbv  
Obs.: 0.35 ppbv

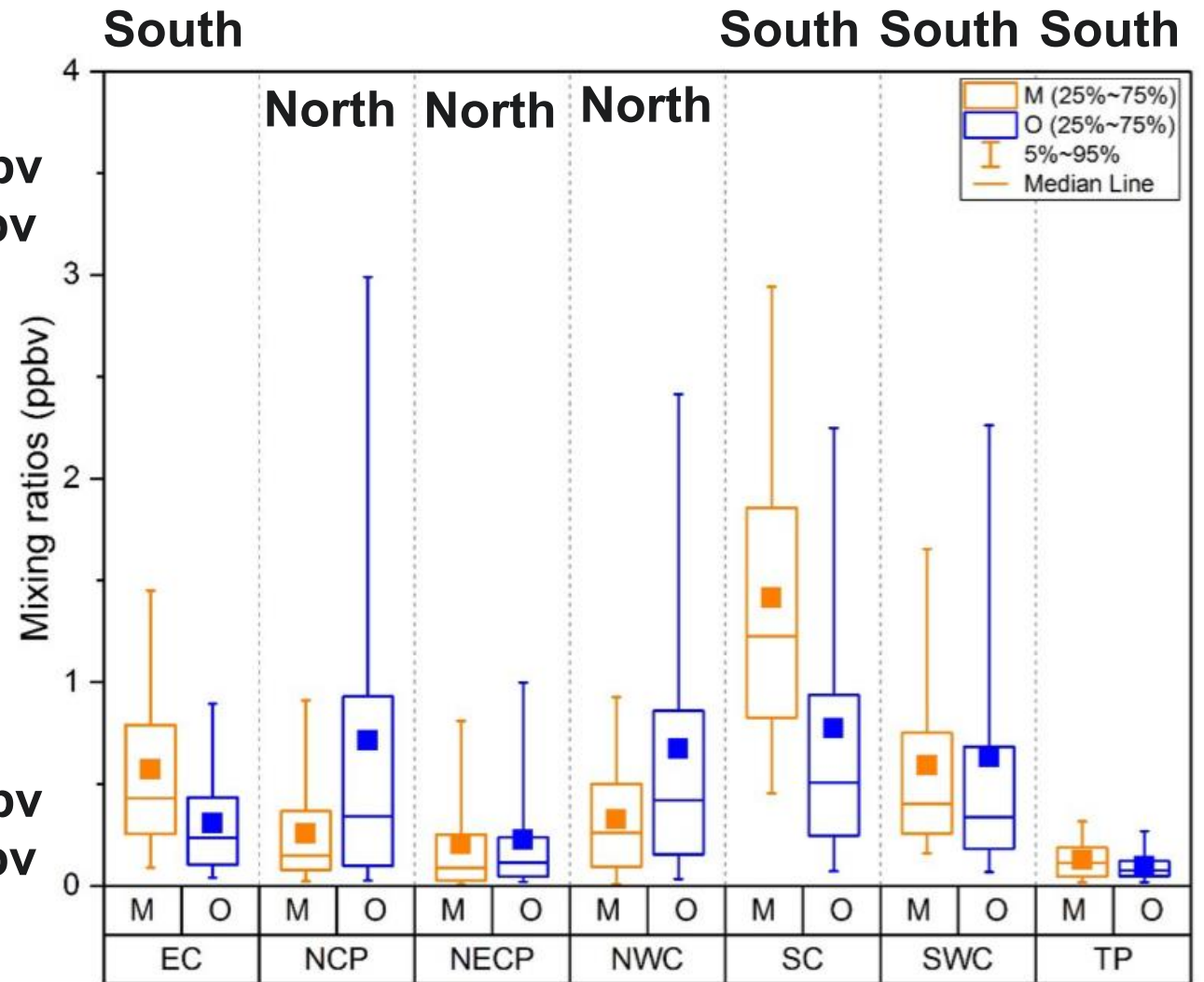
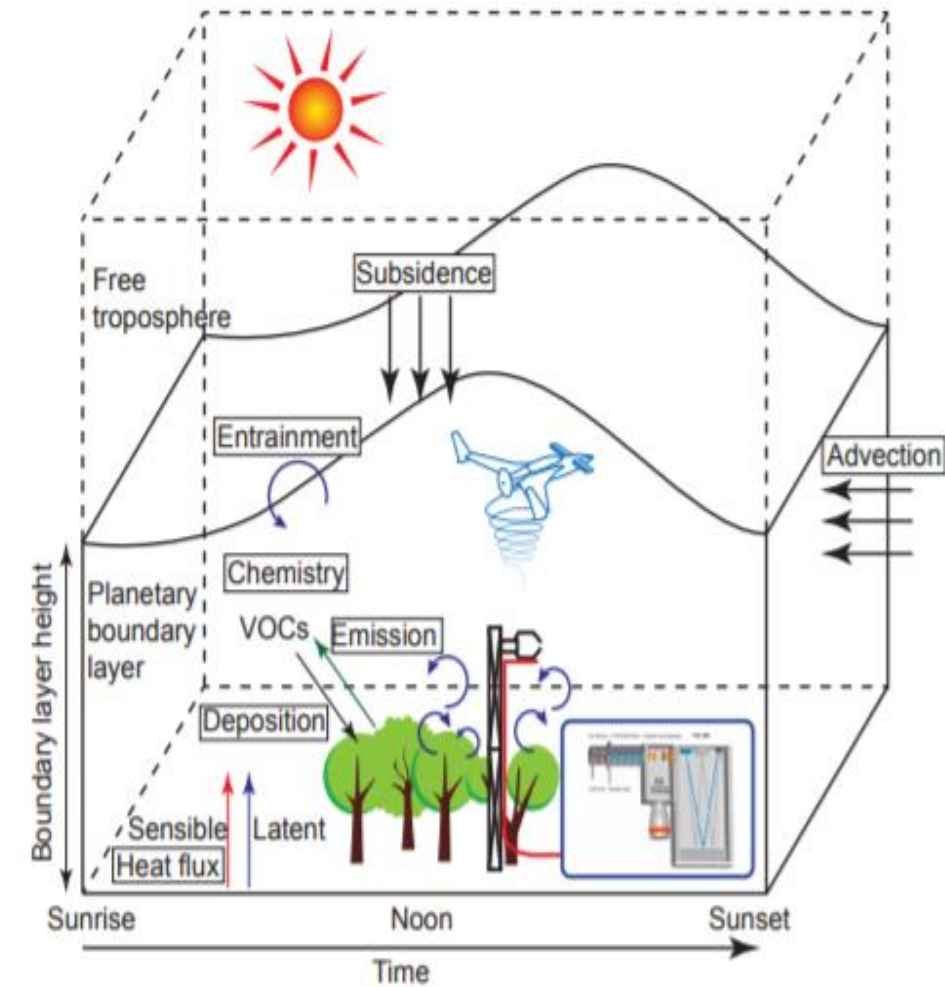
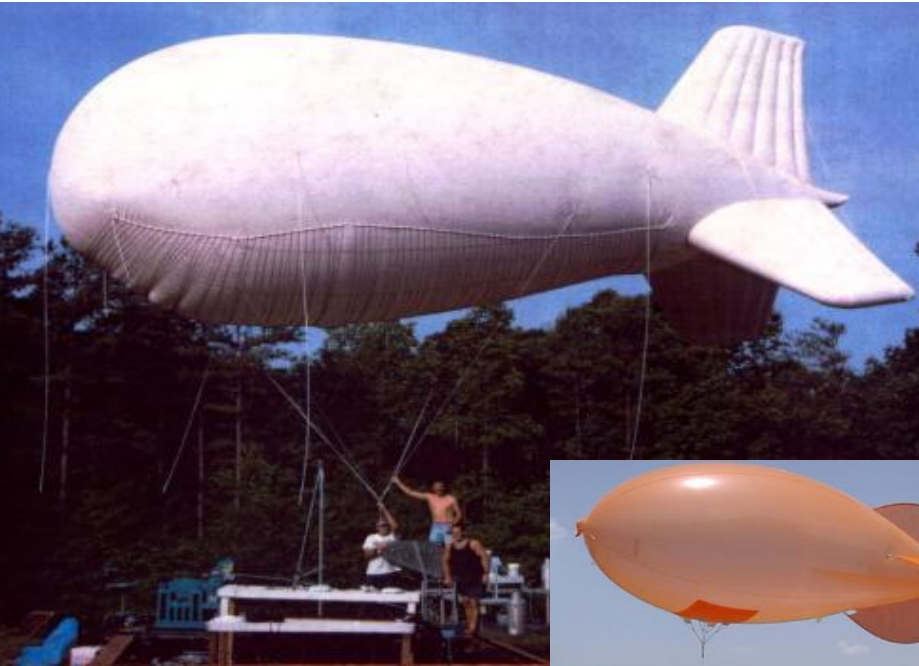


Figure 4. Comparison of isoprene mixing ratios between model simulation and ambient observation in different regions during growing season (May–October).

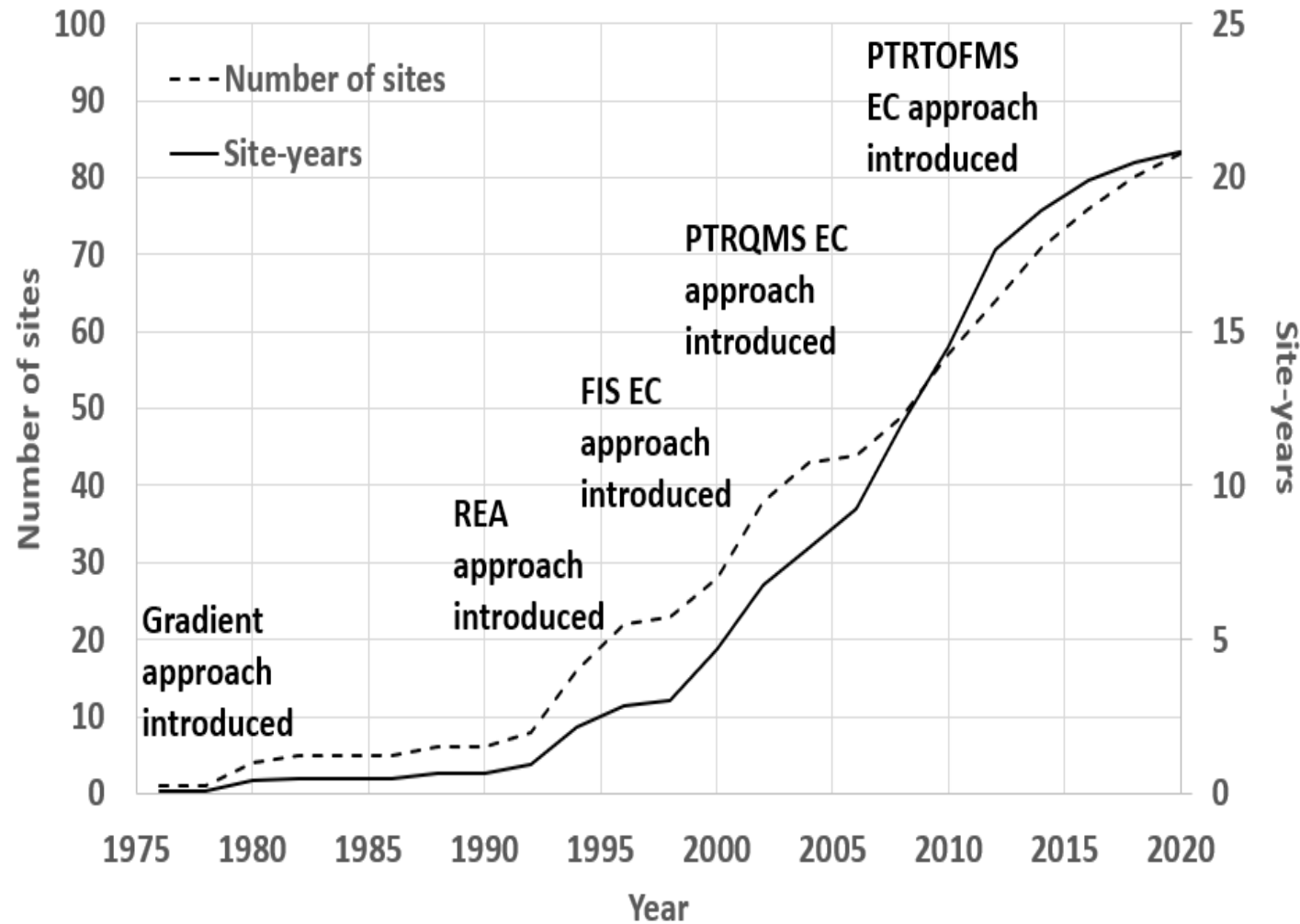
# Atmospheric Boundary layer BVOC measurements



Estimate landscape scale fluxes (~2 to 15 km footprint) using

- Mixed layer vertical gradient
- Mixed layer mass balance

## Direct approach: Long-term, above-canopy BVOC eddy flux data



In 2015:  
FLUXNET CO<sub>2</sub>/H<sub>2</sub>O/energy  
fluxes: 1500 site years of  
data from 212 sites  
(average of 7 years)

BVOC fluxes: 20 site years  
from 65 sites  
(average of < 4 months).

Compared to CO<sub>2</sub>,  
BVOC has 30% of the sites  
but 1.3% of the site years.

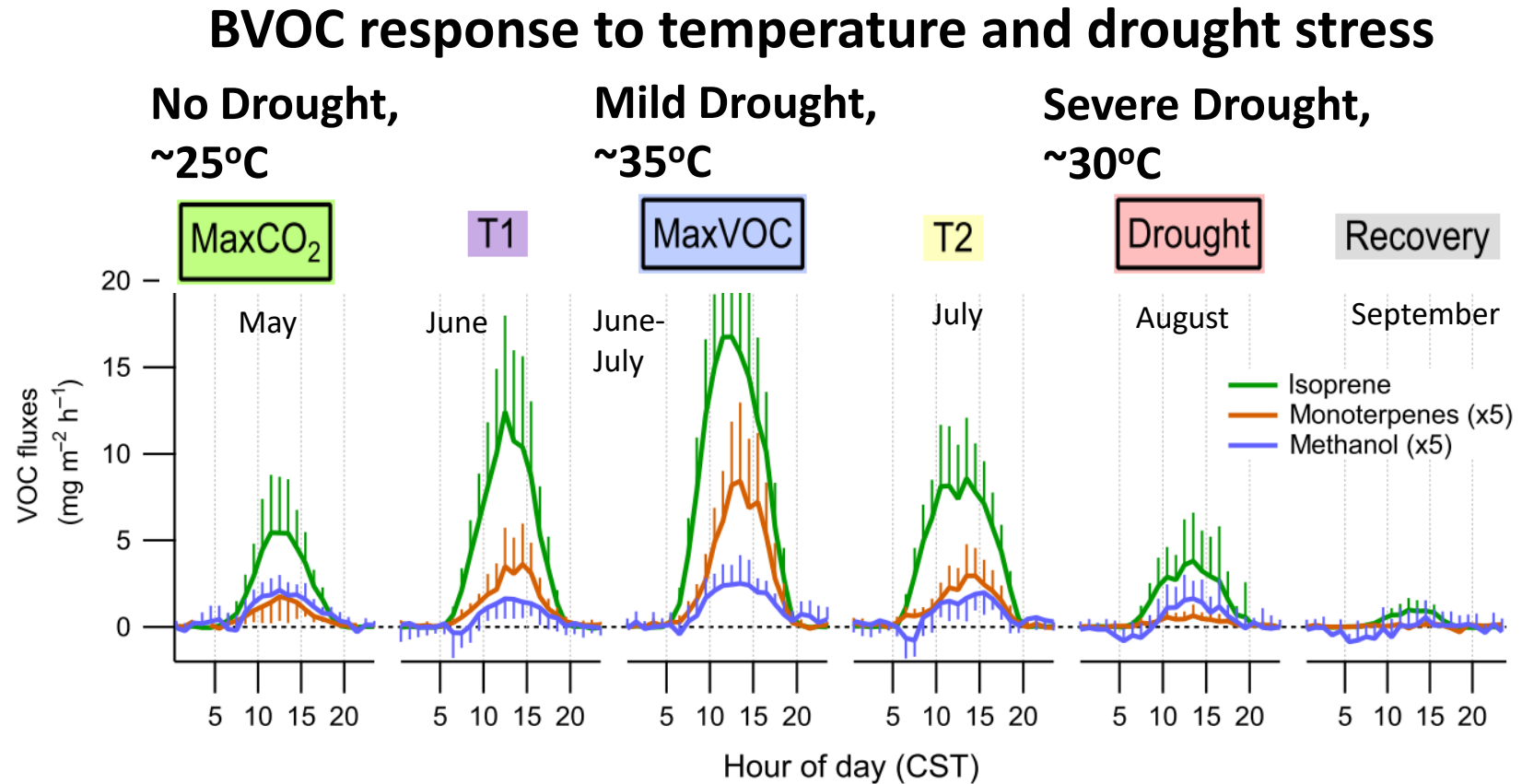
We need networks of low cost, low power BVOC flux systems (e.g., relaxed eddy accumulation with online GC) deployed on existing carbon/water/energy flux towers to provide these observations



# A long-term measurement network can capture a wide range of conditions including extreme events

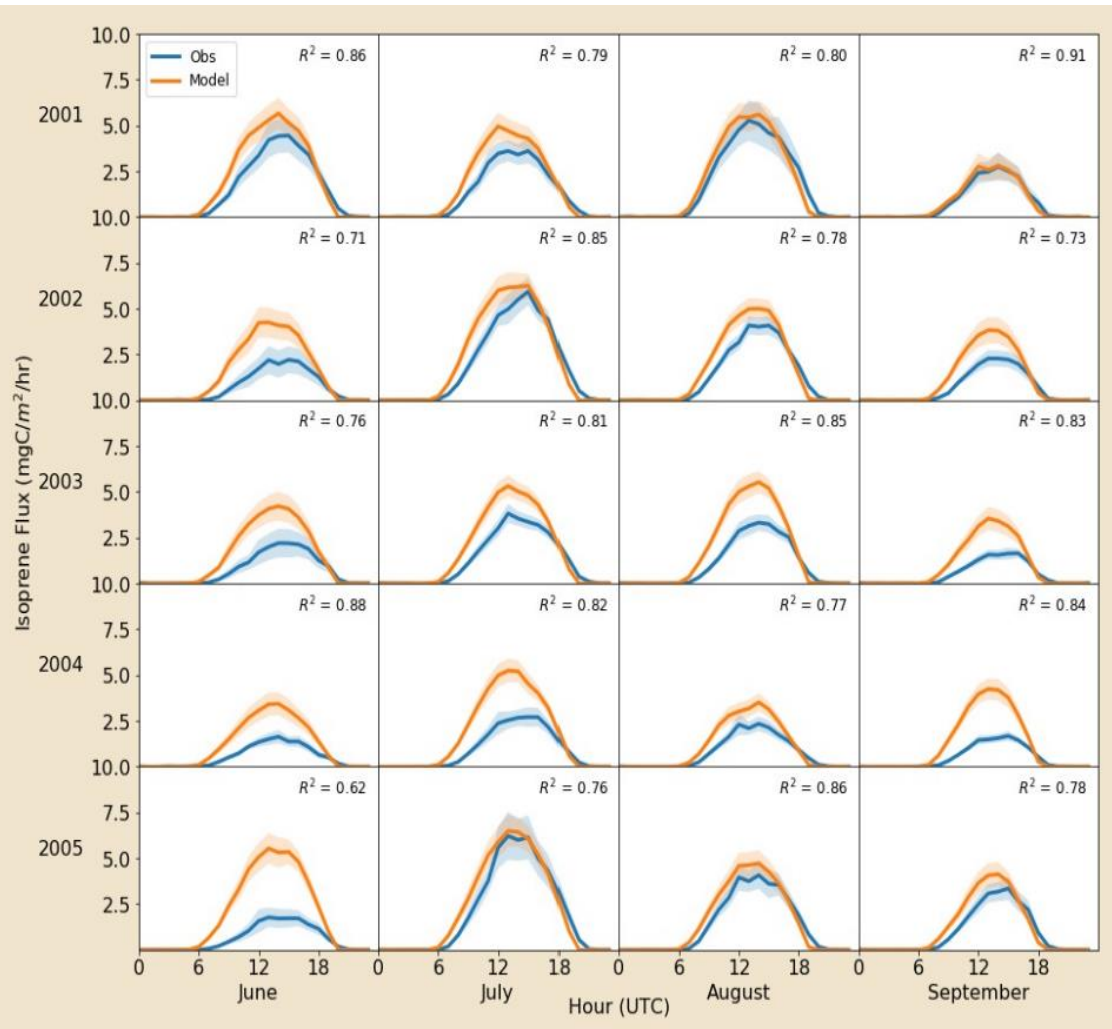


Missouri USA  
2011-2012



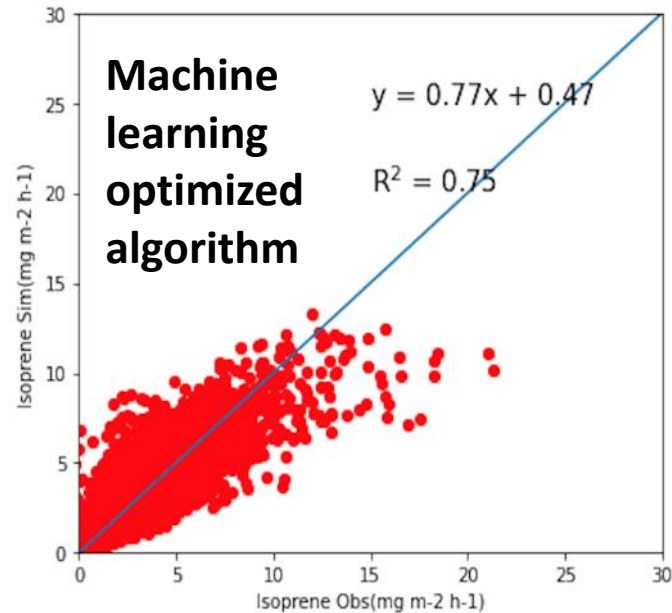
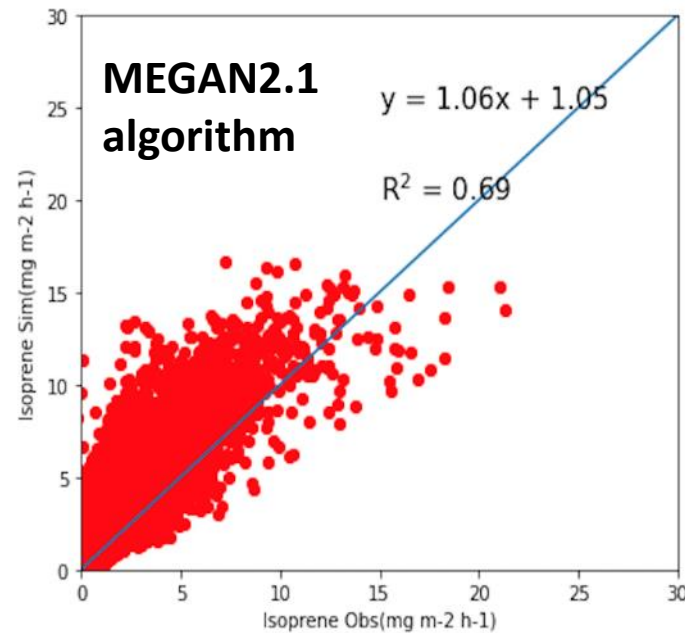
Above-canopy eddy covariance PTRMS flux measurements  
Seco et al. 2015

# Long-term above-canopy flux data: seasonal and interannual BVOC variations



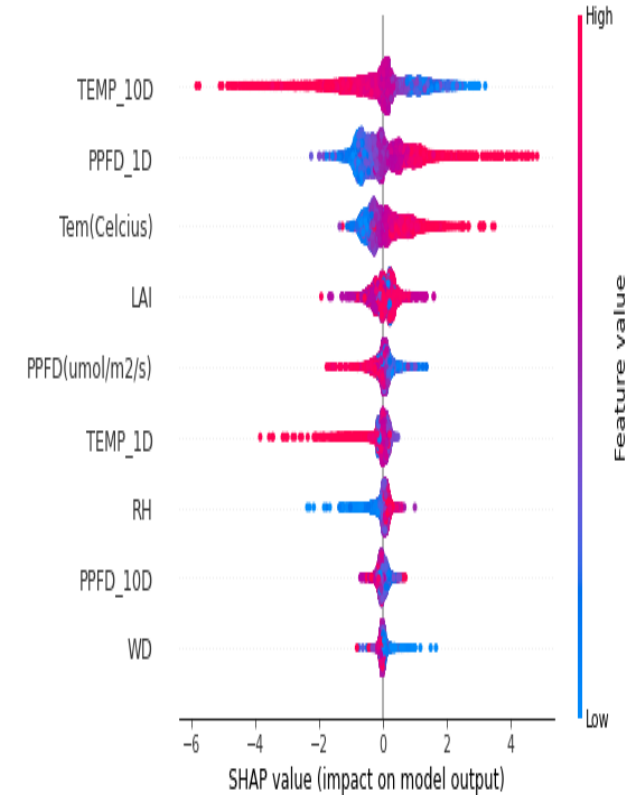
This is the only >2 year BVOC flux dataset.  
Measurements made with relatively low-cost  
fast isoprene sensor observations

Pressley et al. 2005



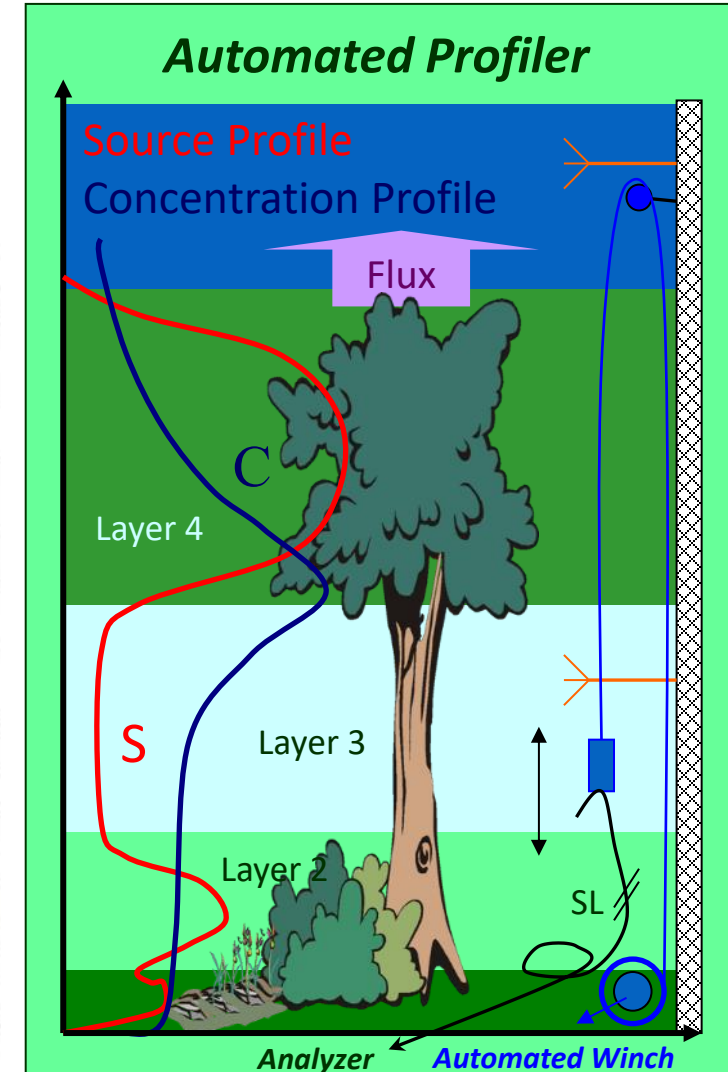
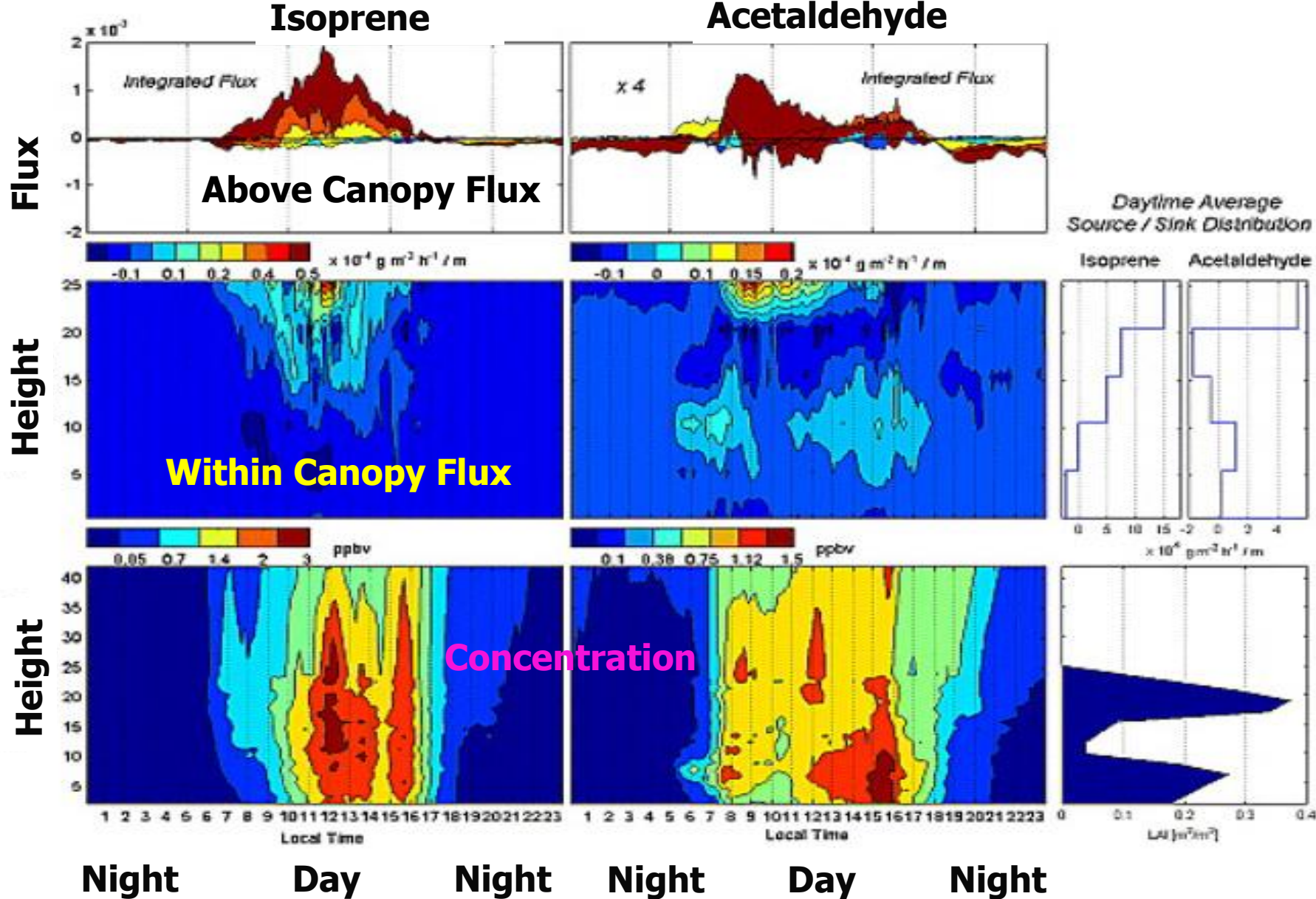
Kittitananuvong et al.

SHAP value identifies  
the most important  
driving variables



Hui Wang

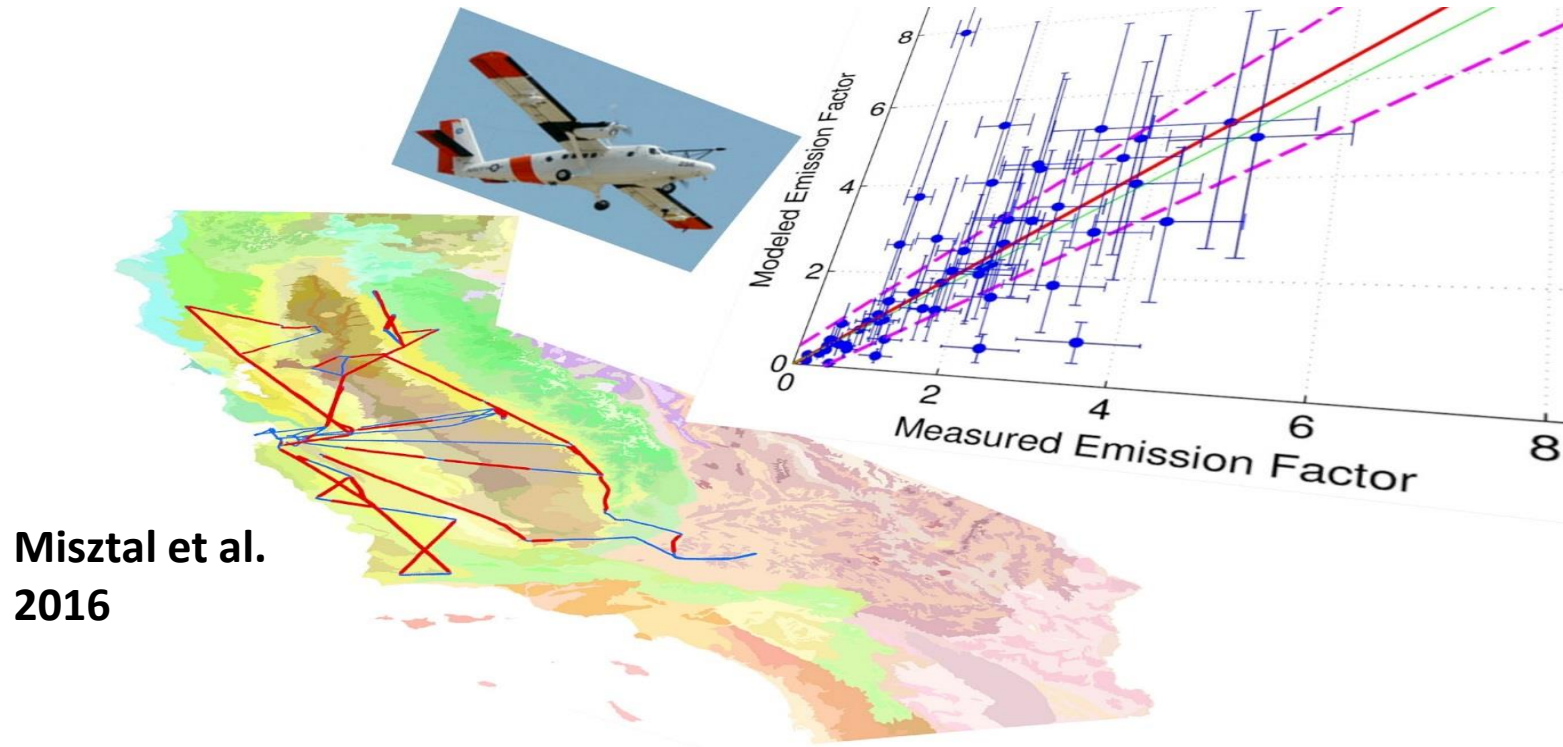
# Canopy scale flux measurements: Within canopy microclimate, chemistry, transport and uptake determine what gets into the atmosphere



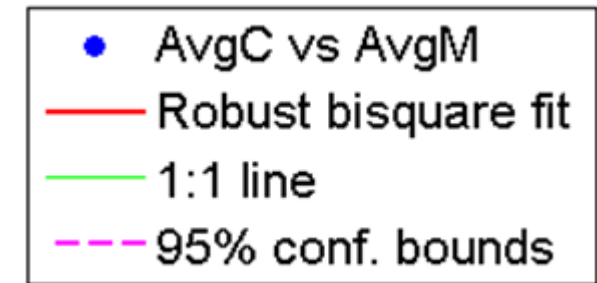
Costa Rica tropical forest  
Karl et al. 2004



# Direct approach: Aircraft flux (EC-PTRMS) measurements to investigate BVOC differences due to landcover change/management



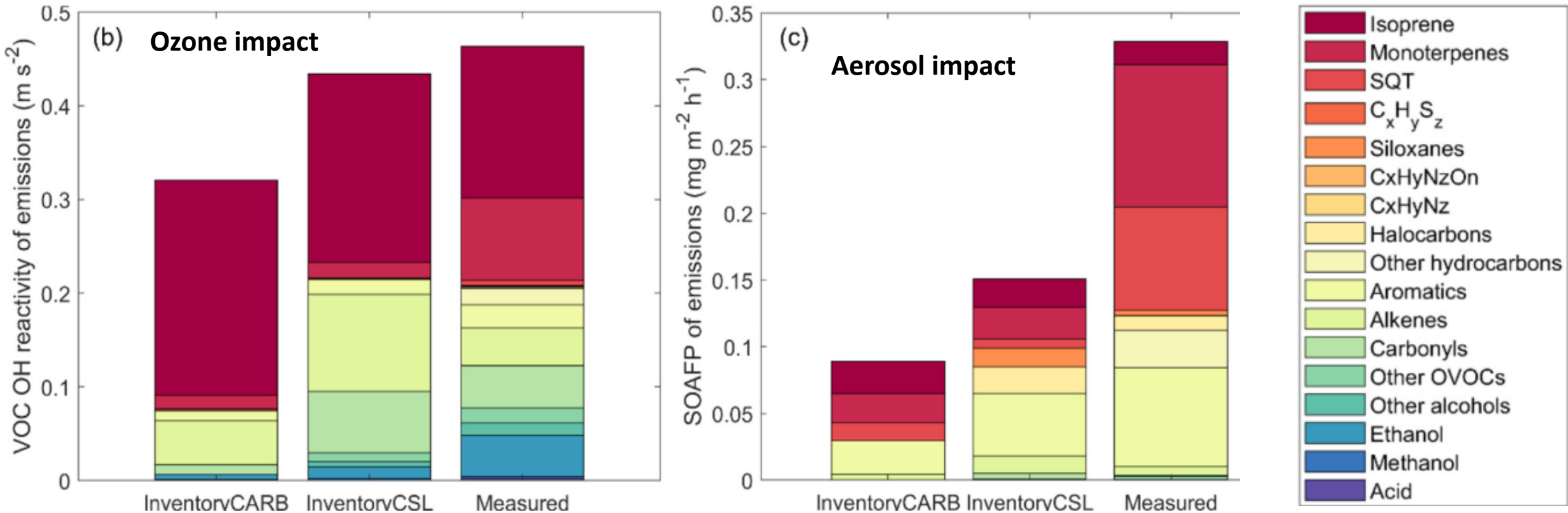
Misztal et al.  
2016



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

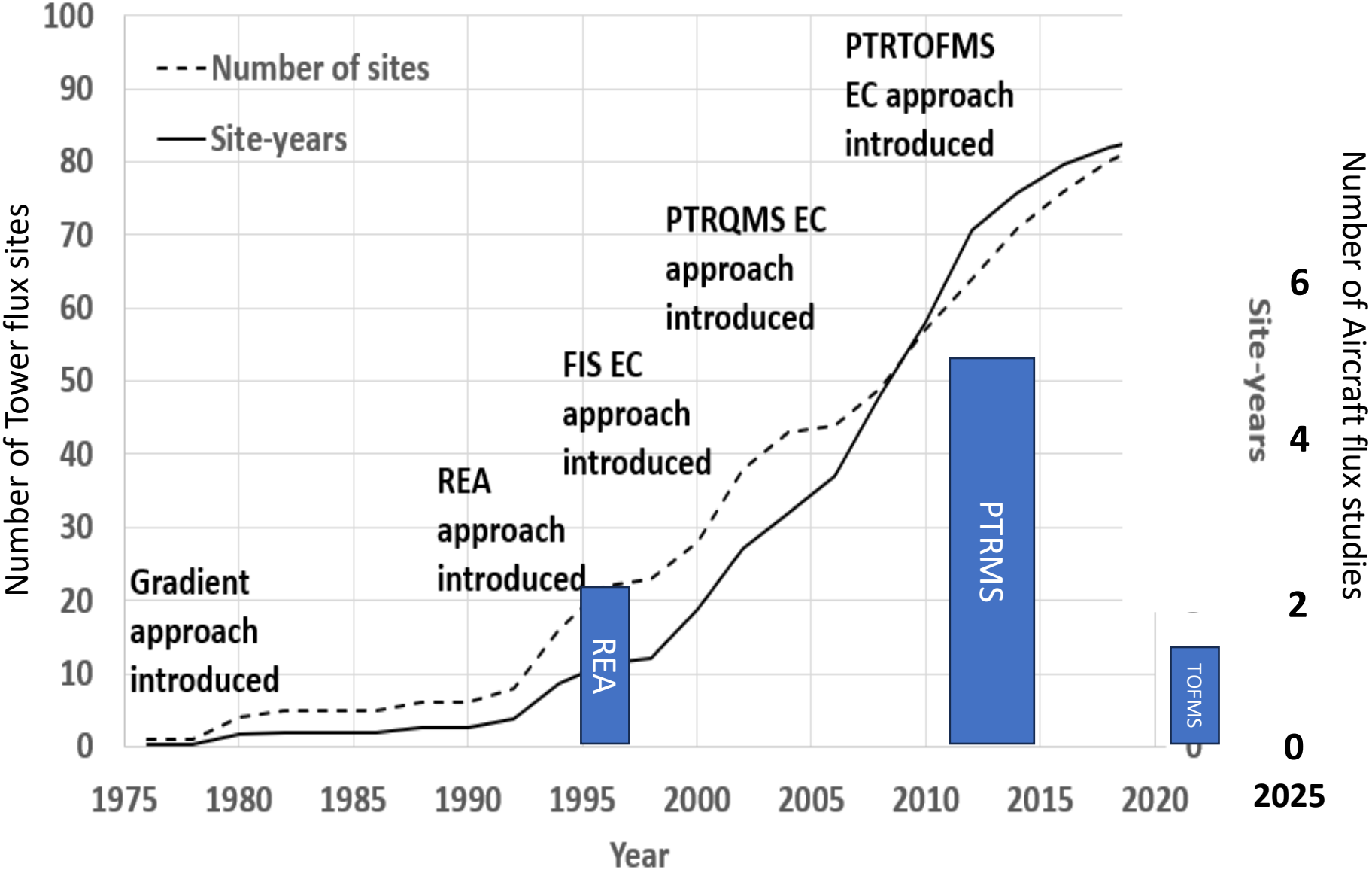
There have been only eight airborne BVOC flux studies:  
5 N. America, 1 Africa, 1 Europe, 1 S. America  
These 8 studies used 7 different aircraft.

# Eddy covariance with PTRTOFMS can measure a wide range of biogenic and anthropogenic VOC fluxes



Los Angeles urban biogenic and anthropogenic VOC fluxes  
Pfannerstill et al. 2023

**Above-canopy BVOC eddy flux data: Tower and Aircraft**  
**Each aircraft study covers an area larger than all tower measurements combined**





## Key Points

1. Reducing ozone below ~100 ppb can be challenging.
2. BVOC emissions from managed (urban, plantations) landscapes can be controlled
3. BVOC emission knowledge gaps (emission factors, assess/monitor) need to be addressed

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**BVOC sampling site: YRD 2009**

**Photo: A. Guenther**