Accounting for the Uncounted:

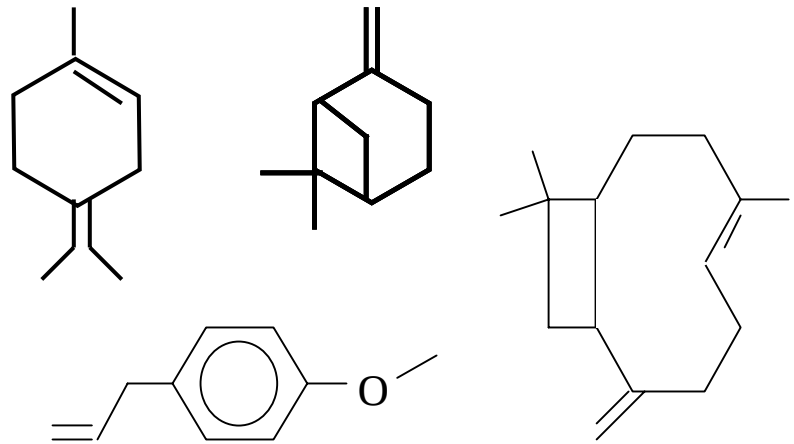
Above Canopy Monoterpene Fluxes and Oxidation Products from Terpene + O_3 Reactions

Anita Lee, Rupert Holzinger, Gunnar Schade, and Allen Goldstein
University of California, Berkeley

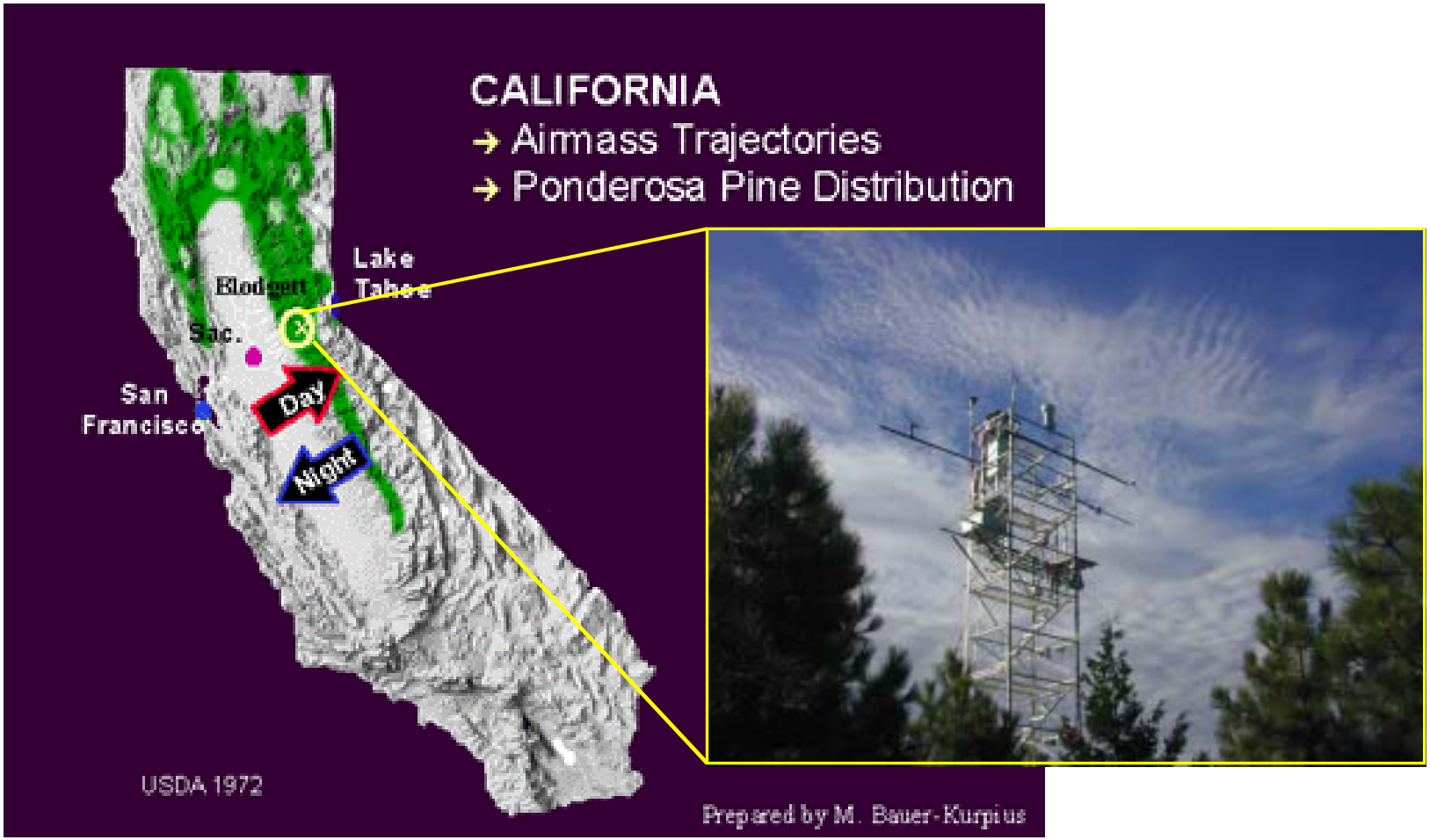
Melita Keywood, Varuntida Varutbangkul, Roya Bahreini, Song Gao, Richard Flagan, and John Seinfeld
California Institute of Technology

What are Terpenes and Why Do We Care?

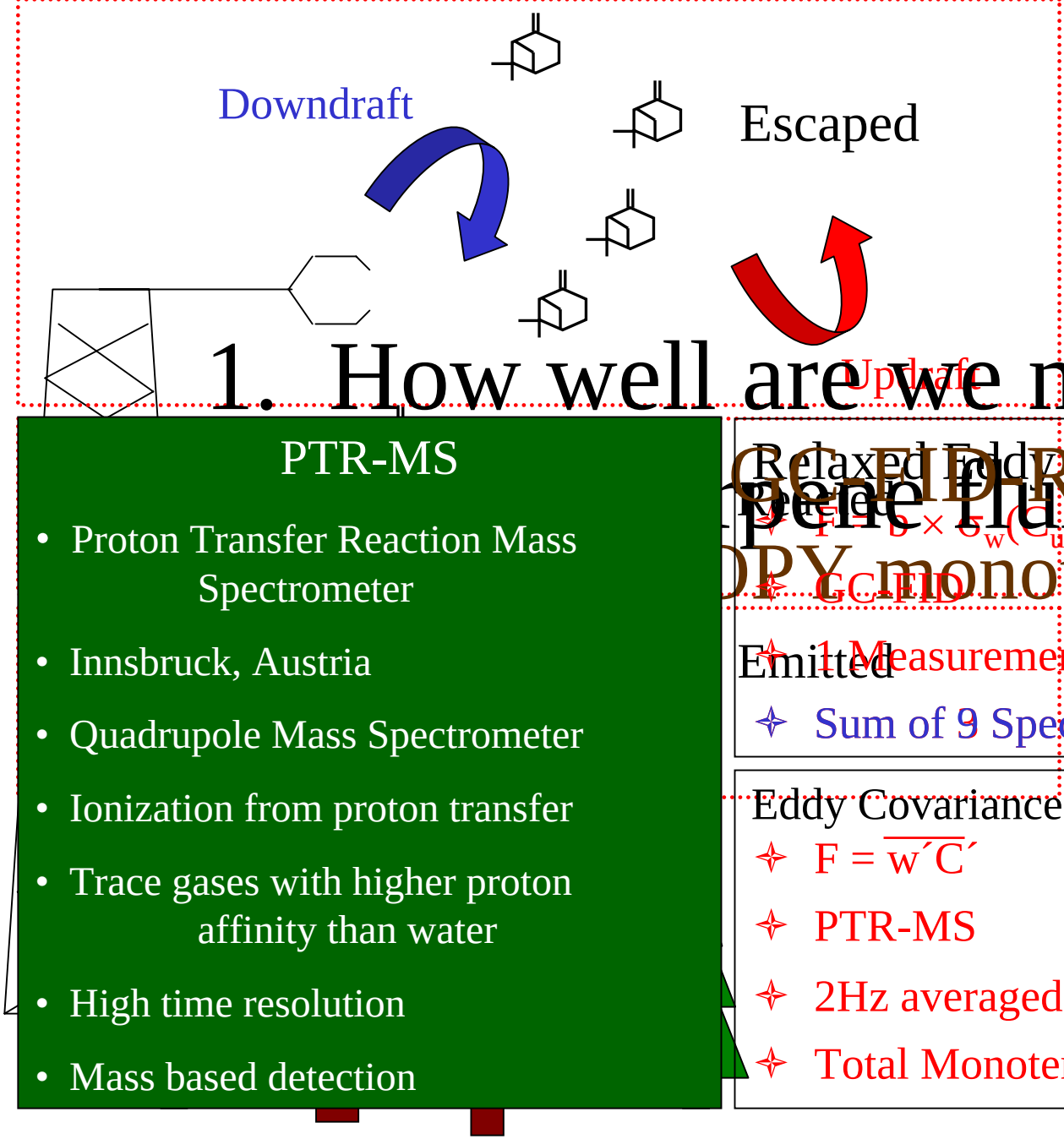
- Monoterpenes ($C_{10}H_{16}$)
- Sesquiterpenes ($C_{15}H_{24}$)
- Oxygenated Terpenes



- Distinctive Smells: Pine, Orange Blossoms, Licorice
- Reactive in the atmosphere
- Role in Tropospheric O_3 Production
- Secondary Organic Aerosol Production



- Ponderosa pine plantation:12 years old, 6m tall
- Western slope of Sierra Nevada (1315m)
- Ameriflux Site: Simultaneous Measurements of CO_2, H_2O, O_3, Aerosol, NO_x, NO_y, ecosystem physiology



Above-Canopy Flux Measurements

1. How well are we measuring plant fluxes?

PTR-MS

- Proton Transfer Reaction Mass Spectrometer
- Innsbruck, Austria
- Quadrupole Mass Spectrometer
- Ionization from proton transfer
- Trace gases with higher proton affinity than water
- High time resolution
- Mass based detection

GC-FID/RGA measure

Relaxed Eddy Accumulation (REA)

$F = b \times \sigma_w (C_u - C_d)$

- GC-FID
- 1 Measurement per hour
- Sum of 9 Speciated Monoterpenes

Oxidation Experiments

Above-Canopy Gradient Measurements

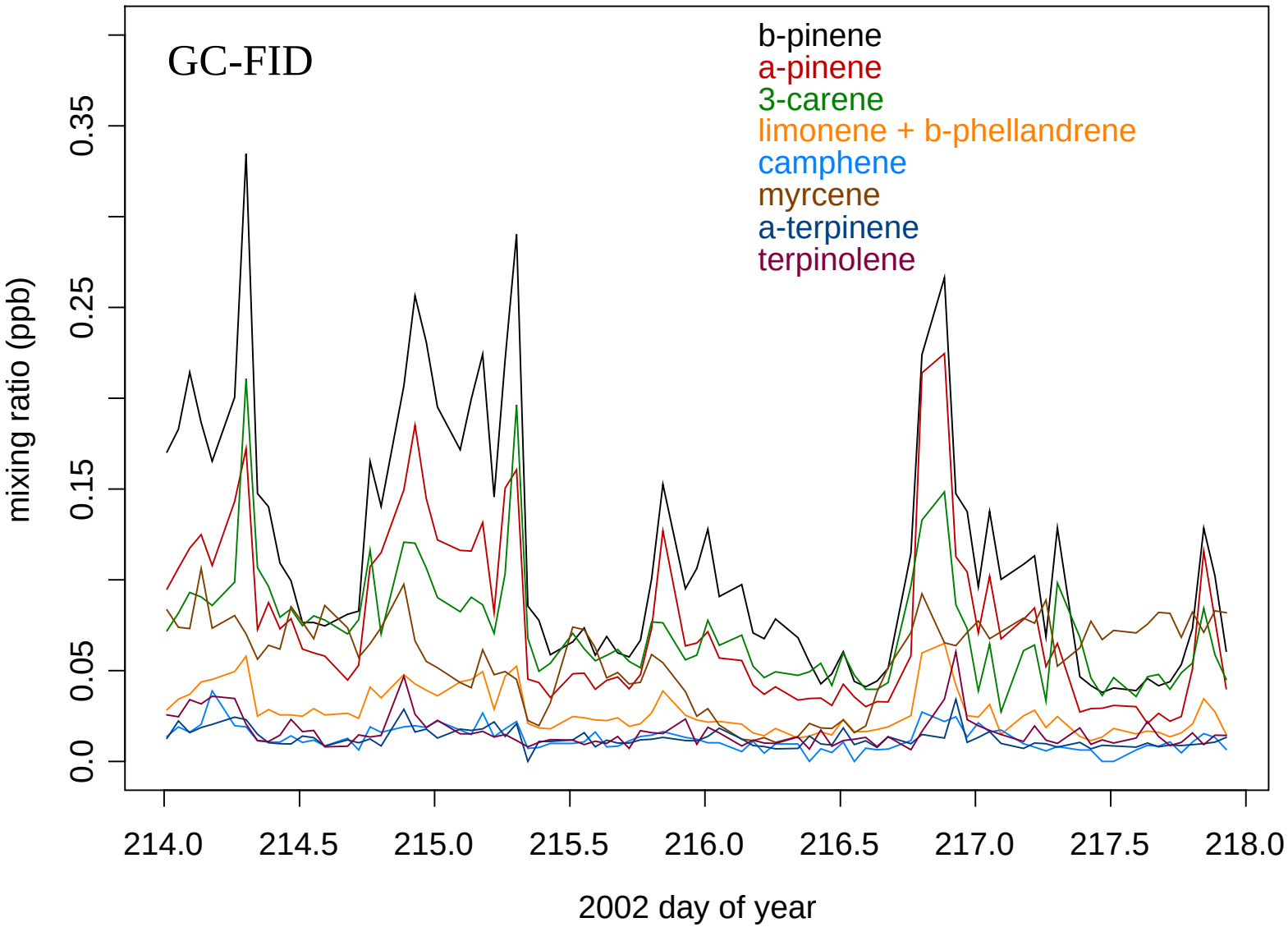
Branch Level Enclosures

Emitted

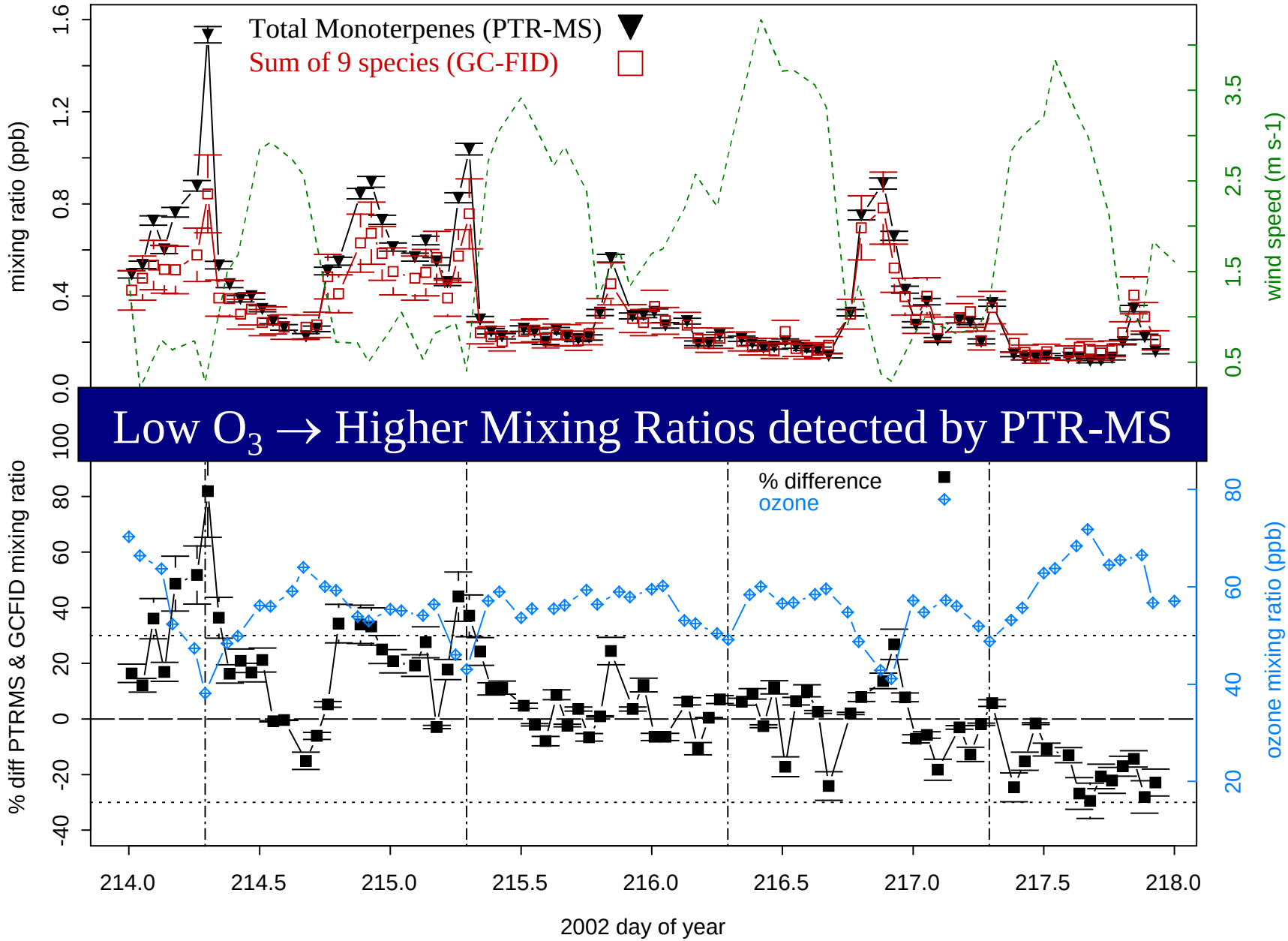
Eddy Covariance (EC)

- $F = \overline{w'C'}$
- PTR-MS
- 2Hz averaged over 30 min
- Total Monoterpenes

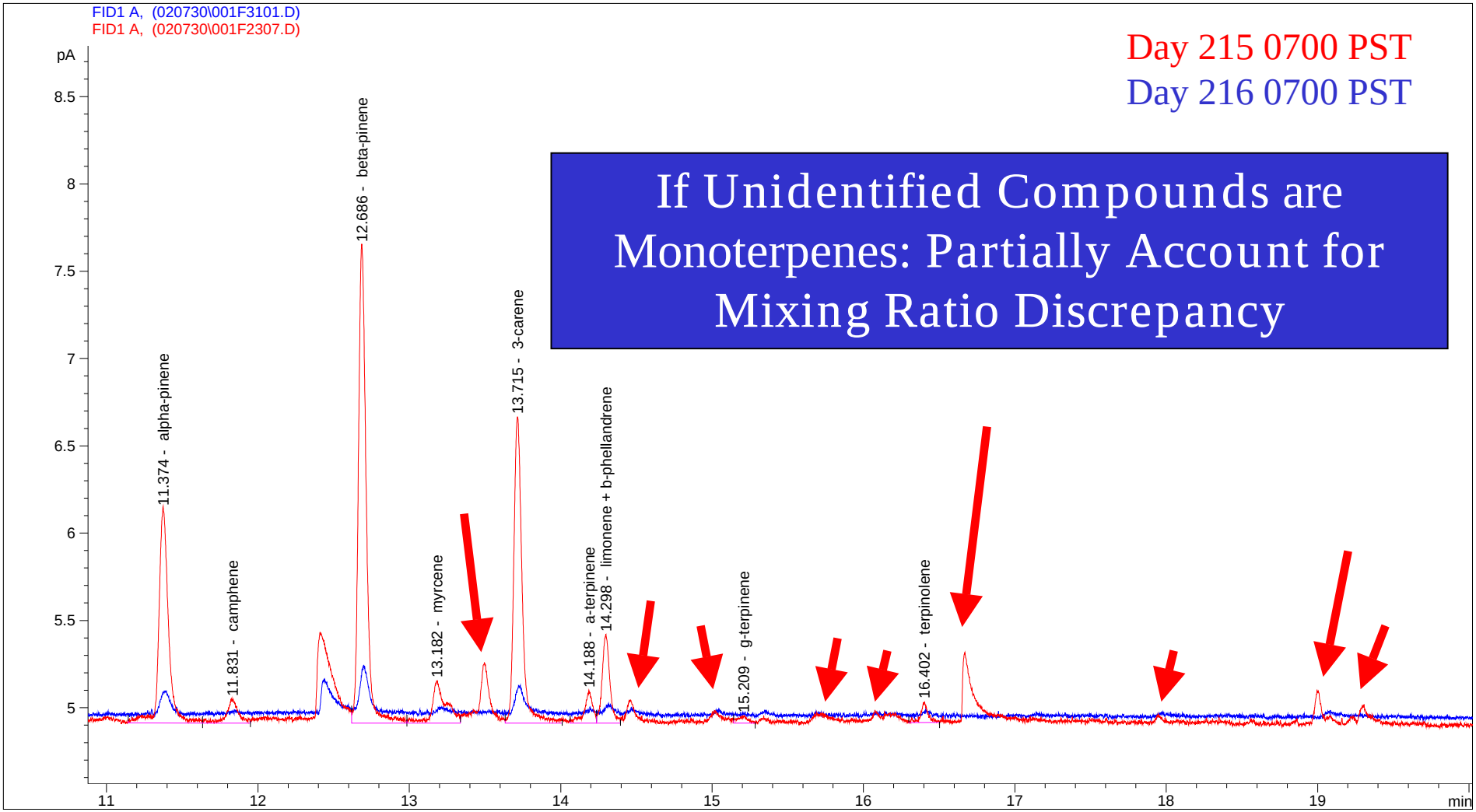
3 Monoterpenes Dominate Measured Mixing Ratio



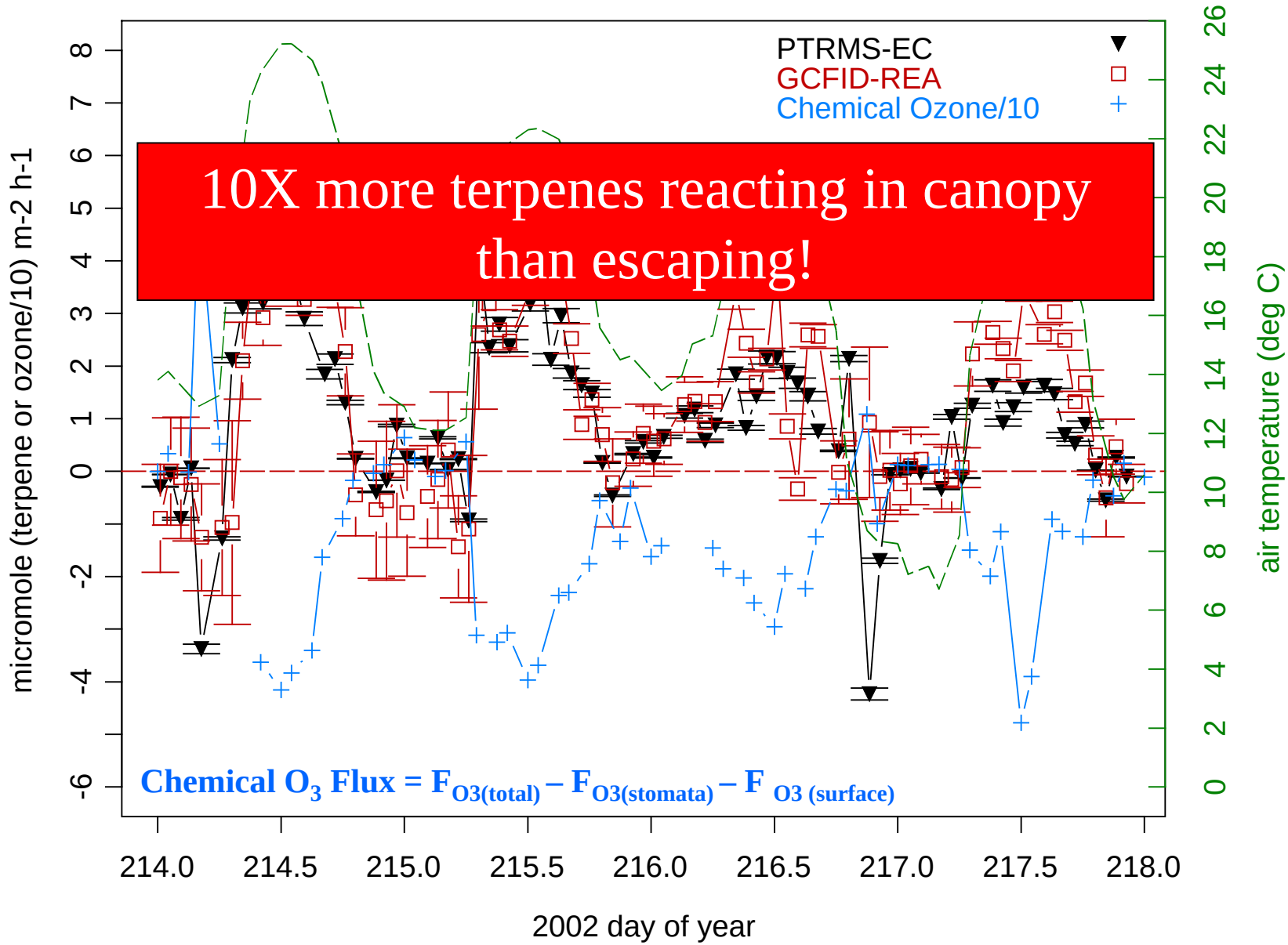
Mixing Ratios Agree Well but Some Periods of Discrepancy



When Mixing Ratios Don't Agree Well . . .
(Day 215 0700 PST)



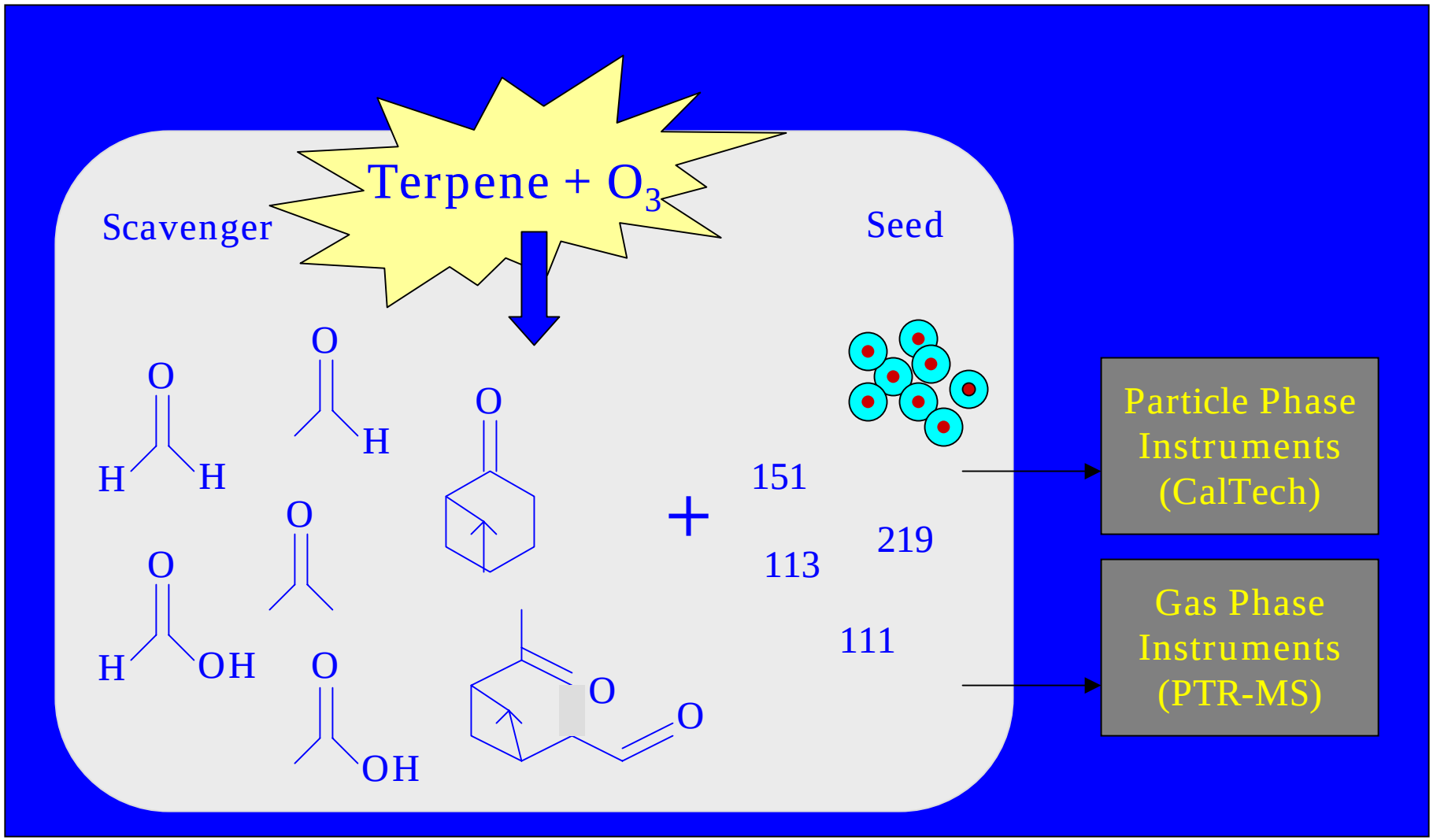
Diurnal Flux Patterns of Monoterpenes and Ozone Agree Well



- Periods of low O_3 → Total monoterpene mixing ratio higher than Σ of known monoterpene species
- Many unidentified compounds detected by GC
- Chemical O_3 flux is 10 times higher than monoterpene flux → 90% of emitted terpenes react inside the canopy

- 2. What is produced when the monoterpenes react with O_3 ?
  - and can we detect them in the canopy?

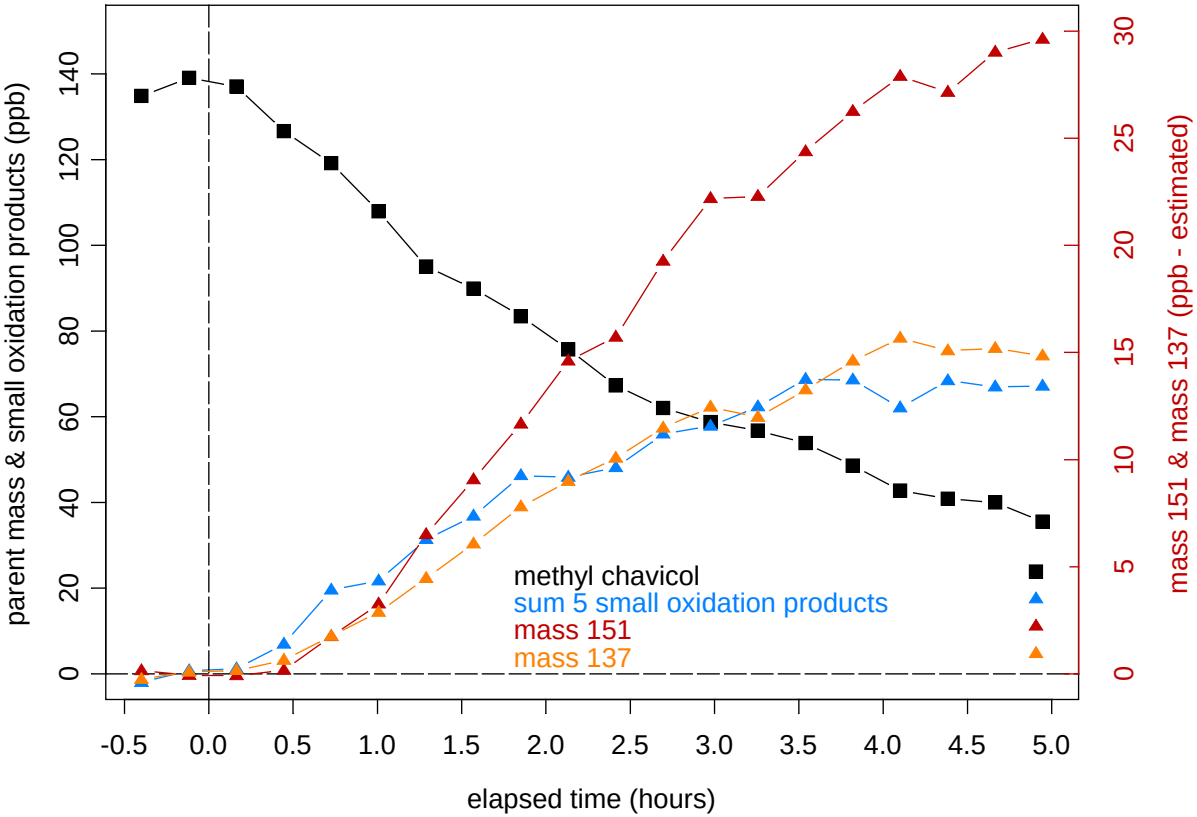
Experimental: Teflon Chambers

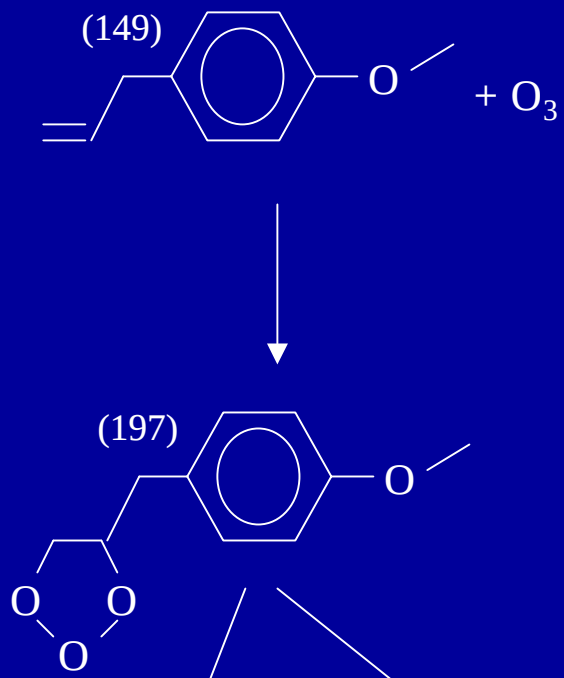


Terpenes

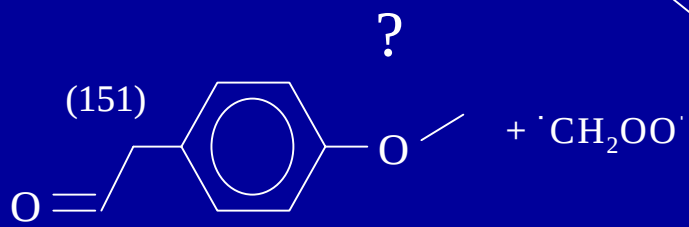
- Oxygenated Terpenes
  - methyl chavicol and linalool
- Monoterpenes
  - terpinolene, α-pinene, β-pinene, 3-carene, α-terpinene, myrcene
- Sesquiterpenes
  - β-caryophyllene and α-humulene

Experiment 1: Methyl Chavicol (4-allylanisole)





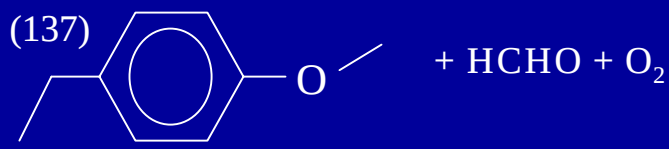
?



4-ethylaldehyde anisole

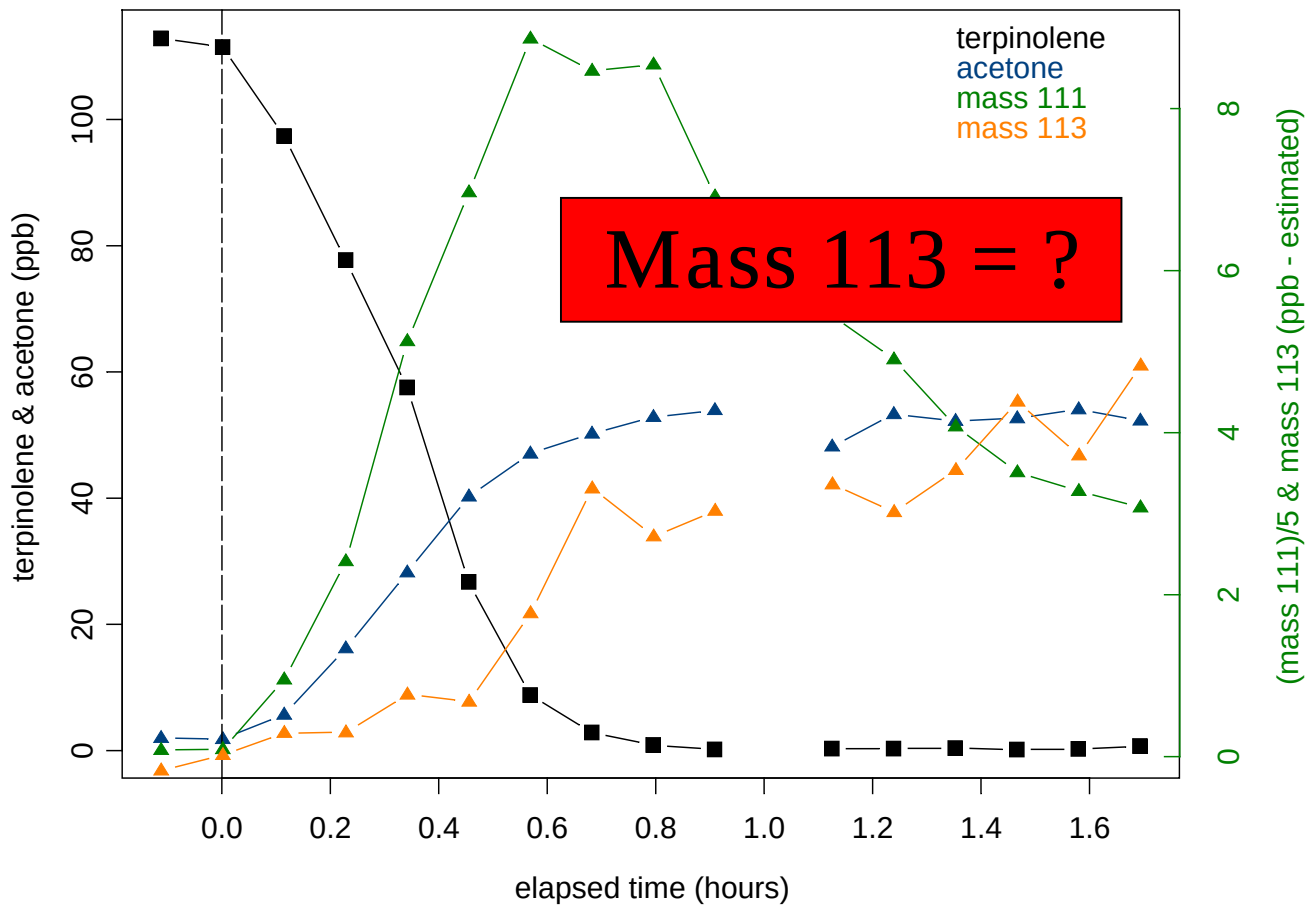
?

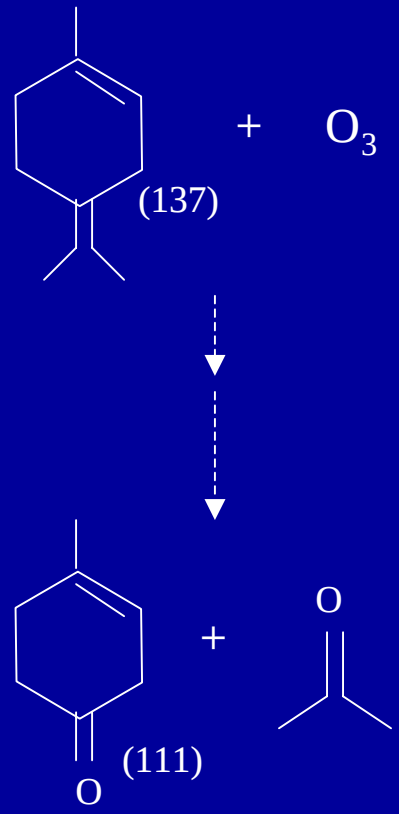
Possible New Oxidation Products



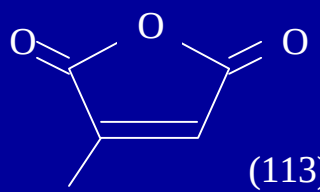
4-ethyl anisole

Experiment 2: Terpinolene





1-Methyl-1-cyclohexen–4-one

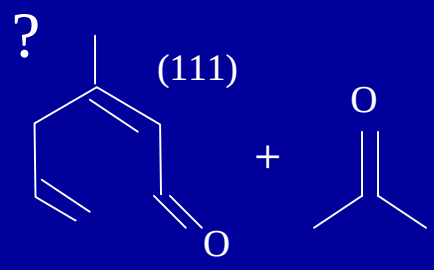


Citriconic Anhydride

(113)

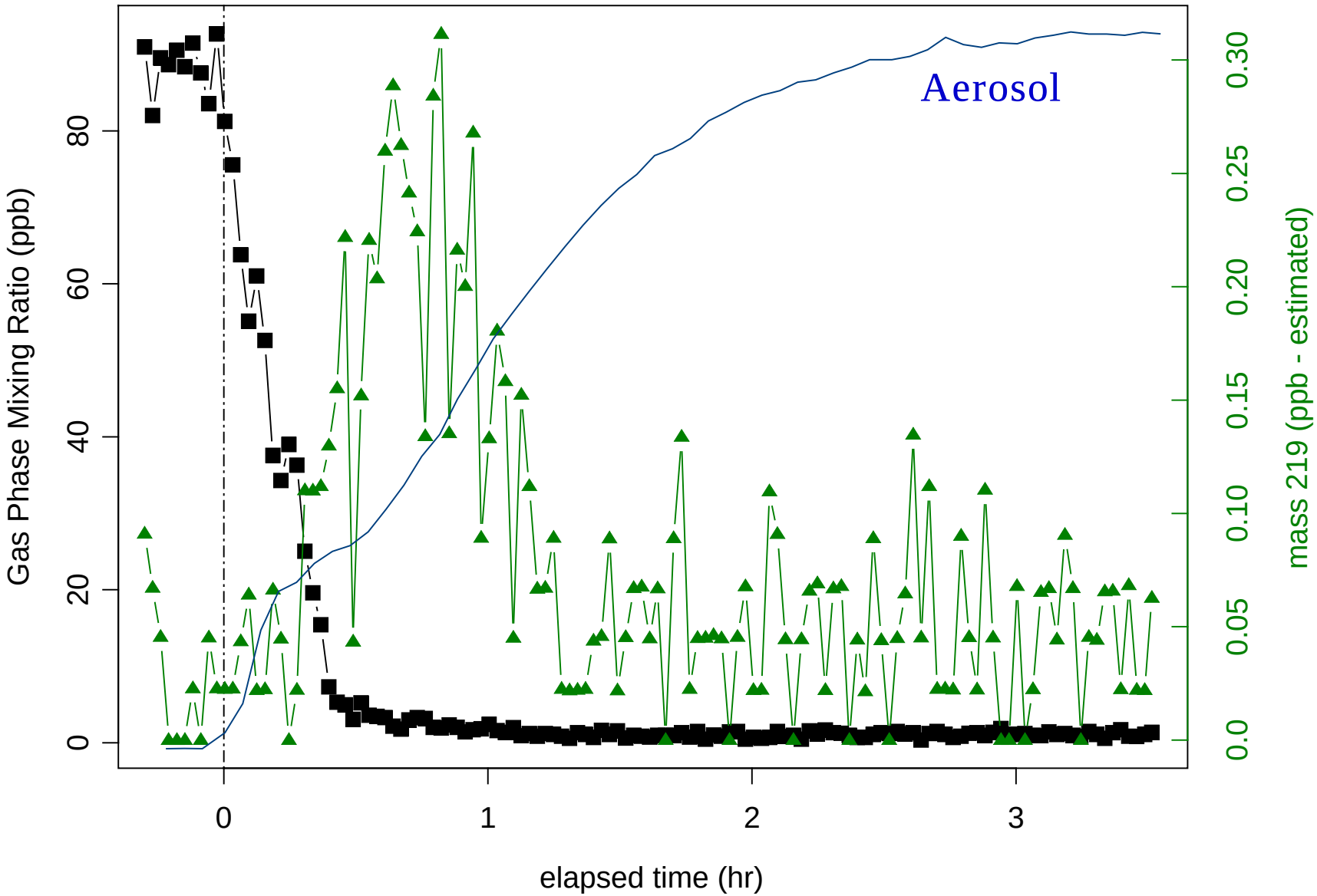
? ?

O_3 +

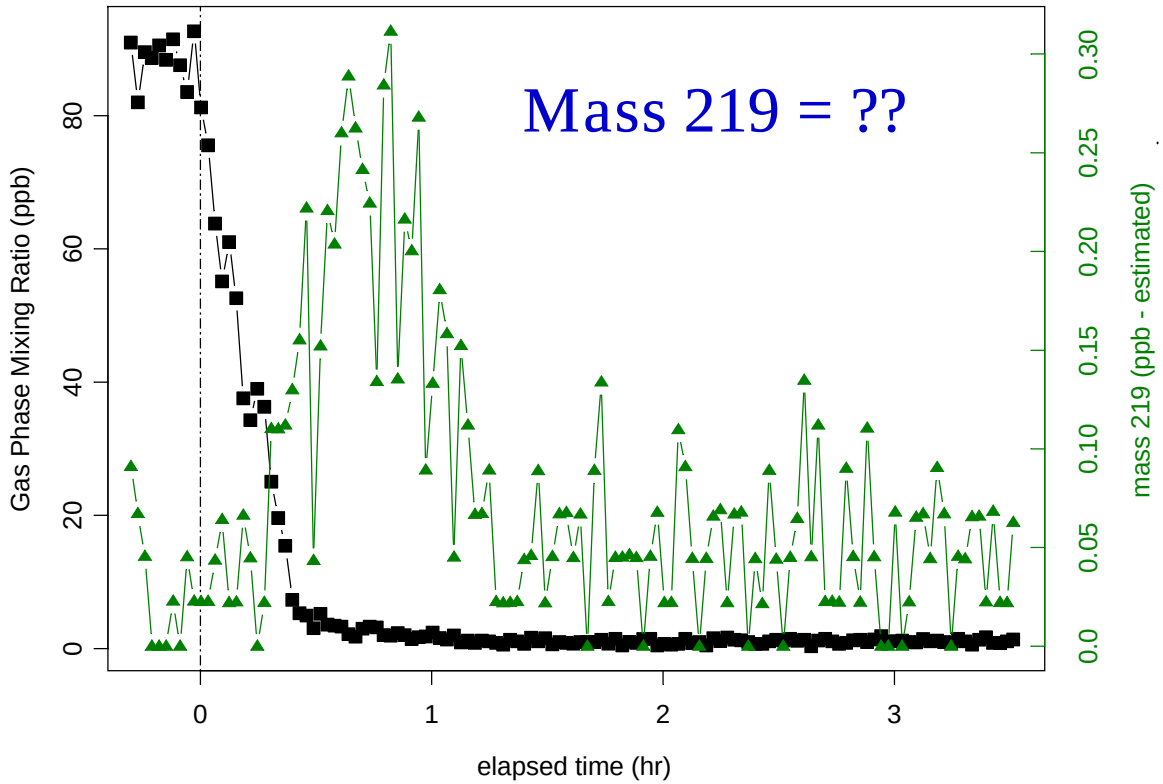


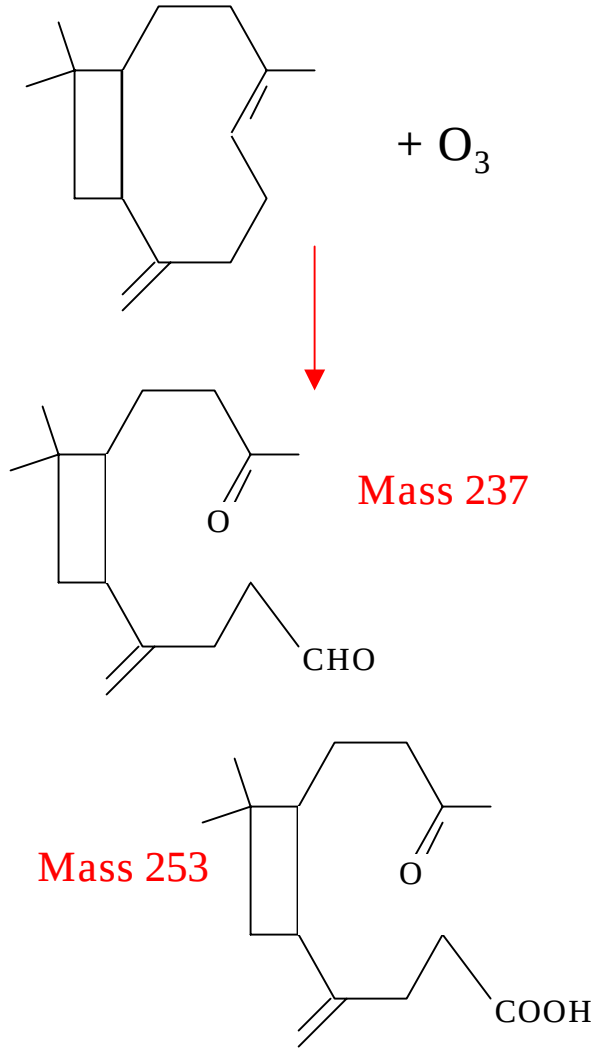
3-Methyl-2,5-hexenaldehyde

Experiment 3: β-caryophyllene

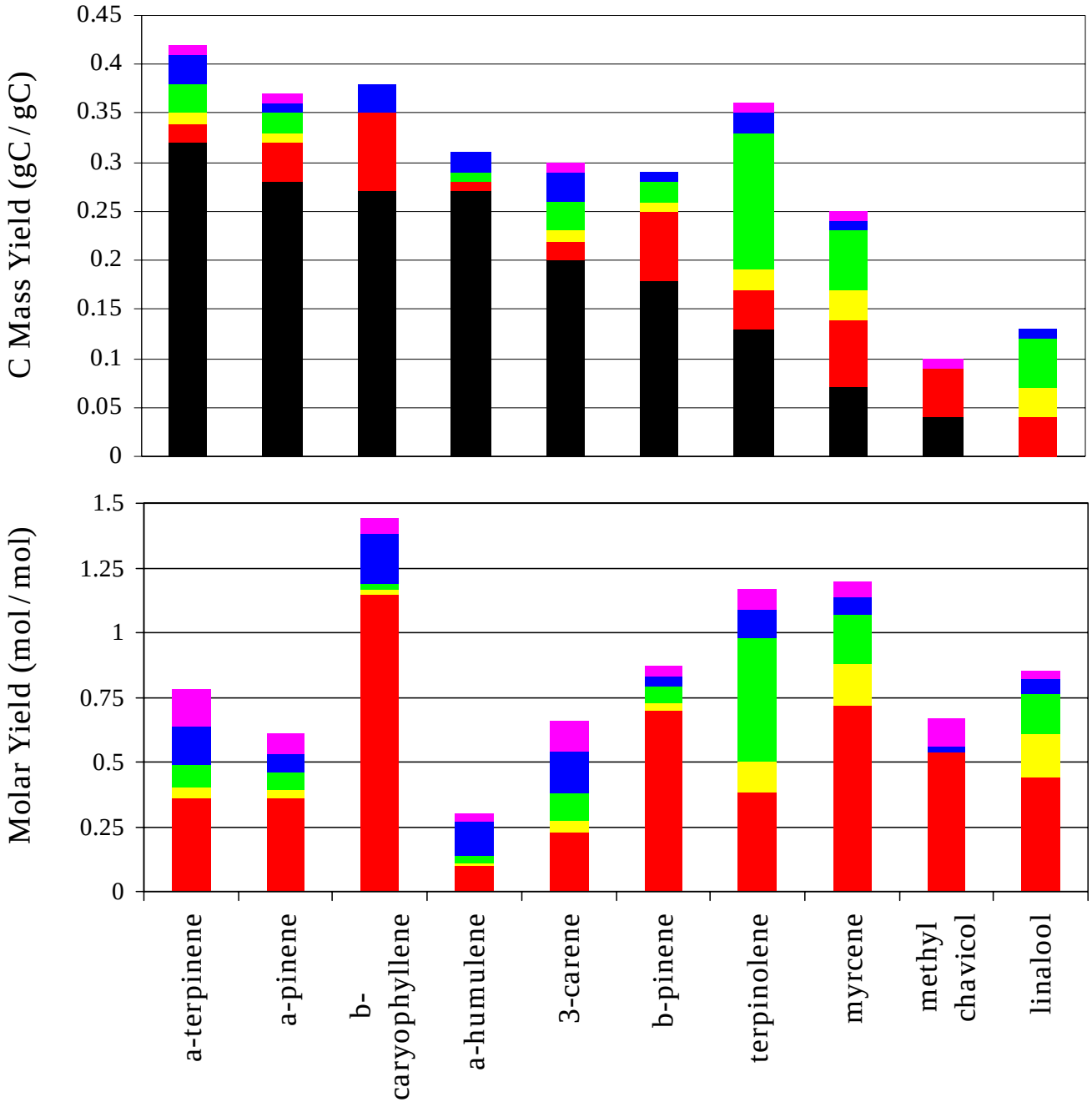


Experiment 3: β-caryophyllene





Calogirou et. al. 1996



Carbon Mass Yield

* Aerosol ~ 60% C

Gas Phase Molar Yield

Series of Terpenes + O_3

- Quantified aerosol yields
- Quantified upper limit yields of small oxidation products!
- New tentative identification of larger oxidation products
- Observed Multi-step Oxidation and Product Formation

Mixing Ratios and Fluxes by GC FID-REA and PTR-MS-EC compare well and are 10 times lower than chemical O_3 flux

10%

Chemistry involving O_3 & unidentified terpenes.

90%

Can we detect the oxidation products in the canopy?

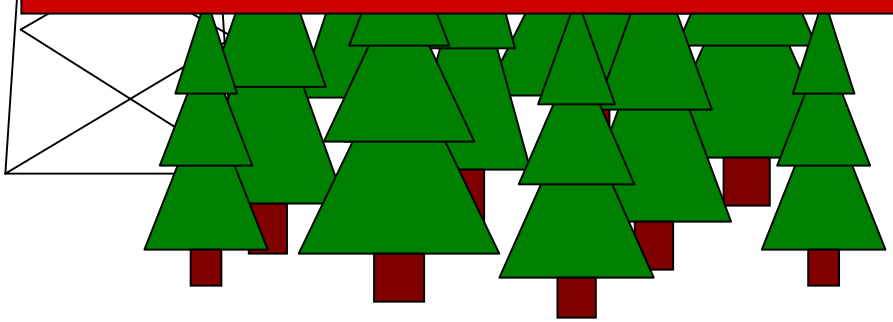
What is emitted is not the same as what escapes the canopy?

Above-Canopy Flux Measurements

Oxidation Experiments

In-Canopy Gradient Measurements

Branch Level Enclosures



What have we learned?

The story continues . . . (but not today)

- In – canopy gradient measurements (Holzinger et al. submitted to ACP)
- Branch-level enclosures (in prep.)
- Full photochemical oxidation experiments
  - Terpene + OH + O_3 + NO_x + hν
- Improve estimates of global VOC emissions, SOA production, and secondary production of acetone, formaldehyde . . .

Thank you!

DOE-GCEP:

Jeff Gaffney, Milt Constantin, Mary Kinney

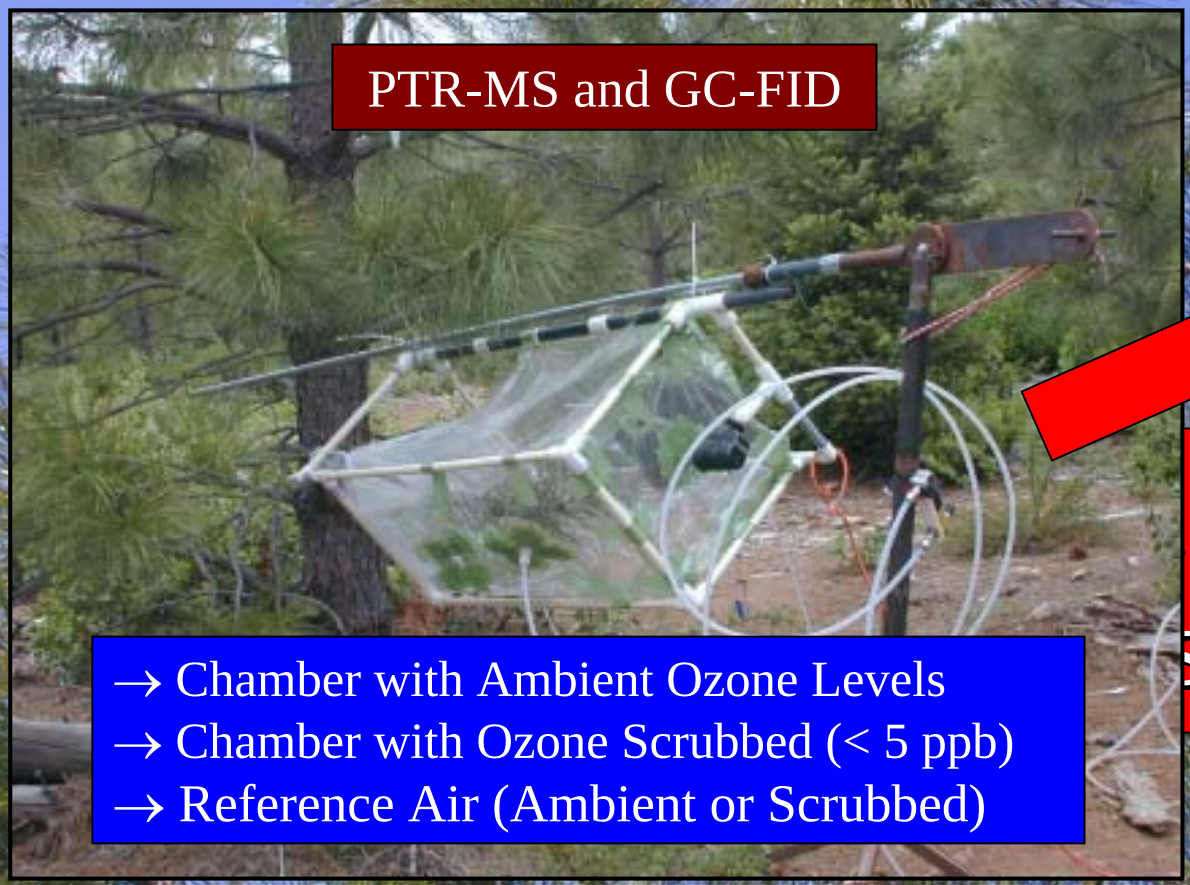
NSF

California Air Resources Board

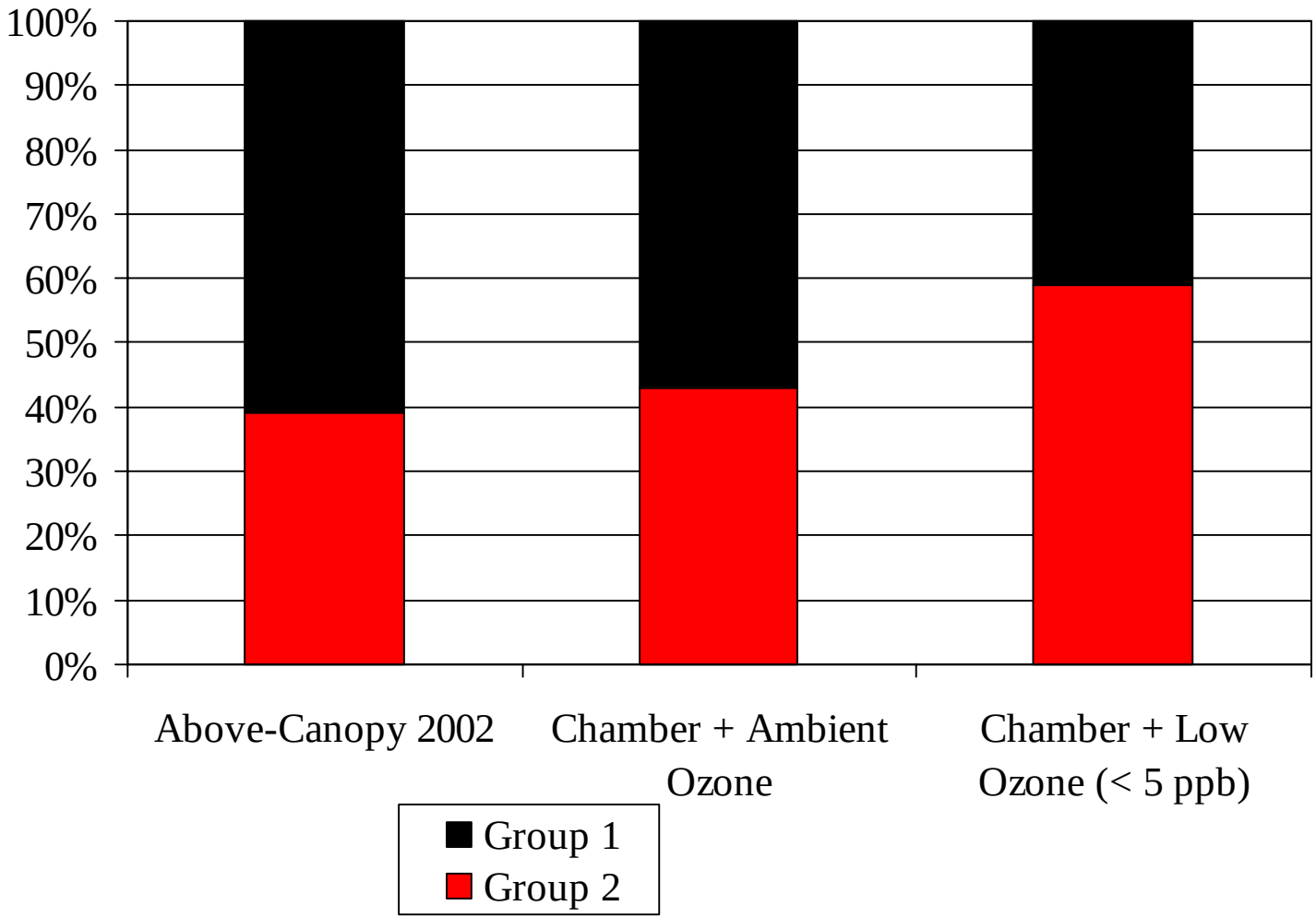
Blodgett Forest Crew


Questions???

Do Above-Canopy Measurements of Escaped Monoterpenes Match Emissions at Branch Level?



Reduced O_3 Levels Increase Relative Percentage of Shorter–lived Monoterpenes



Group 1:

α-pinene
β-pinene
3-carene

~ longer τ

Group 2:

limonene
β-phellandrene
camphene
myrcene
terpinolene
α-terpinene
γ-terpinene
Σ 10 unknowns

~ shorter τ

Molar Yields from Unidentified Masses (m/z) Produced from Terpene + Ozone Oxidation Reactions