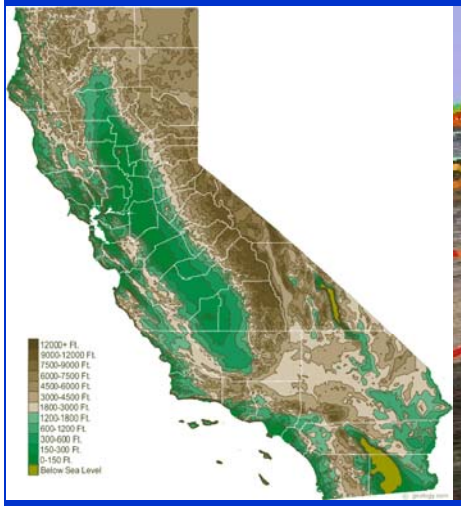
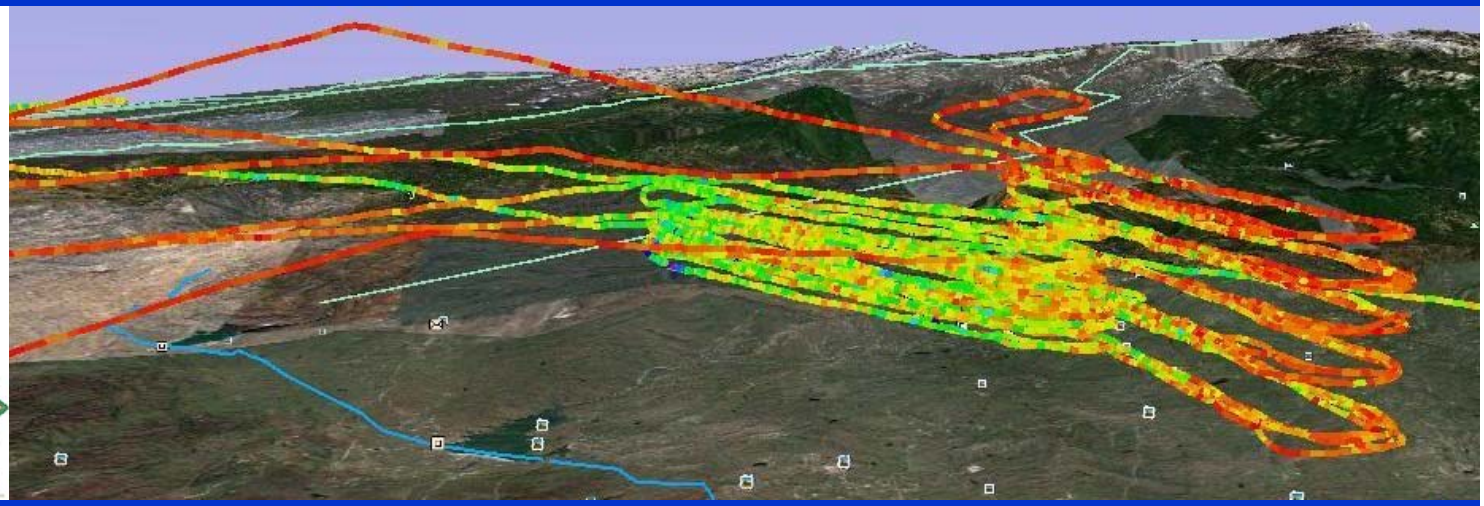
Evaluation of regional isoprene emission estimates in California





Principal Investigator: Allen Goldstein[1]

Staff: Pawel Misztal[1], Robert Weber[1]

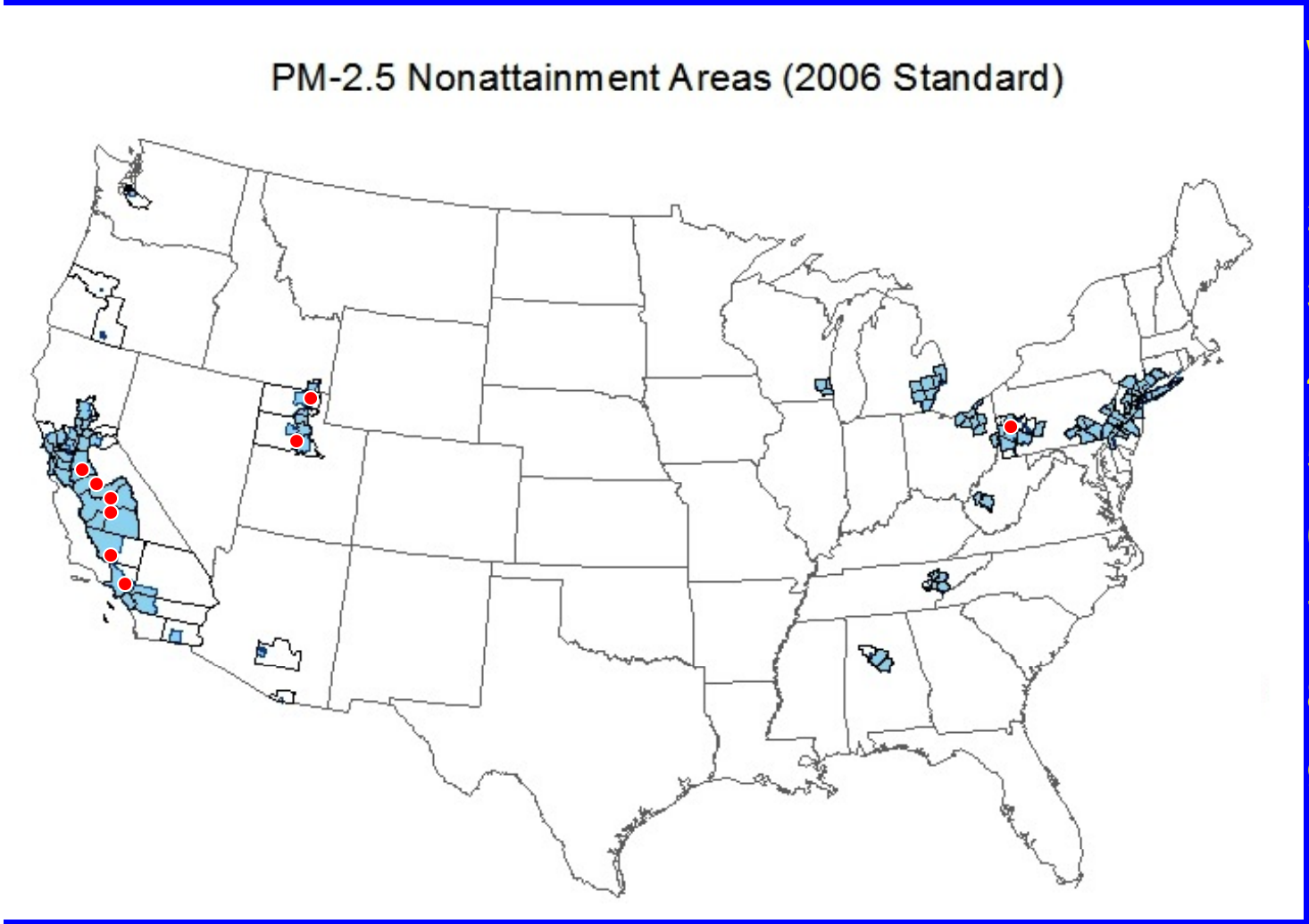
Co-PI: Alex Guenther[2]

Collaborators: Thomas Karl[2], Haf Jonsson[3], Jeremy Avise[4], Klaus Scott[4]

(University of California at Berkeley[1], National Center for Atmospheric Research[2], Naval Postgraduate School[3], California Air Resources Board[4])

Acknowledgements: California ARB, NOAA, Center for Interdisciplinary Remotely-Piloted Aircraft Studies

PM2.5 Nonattainment Areas in U.S.

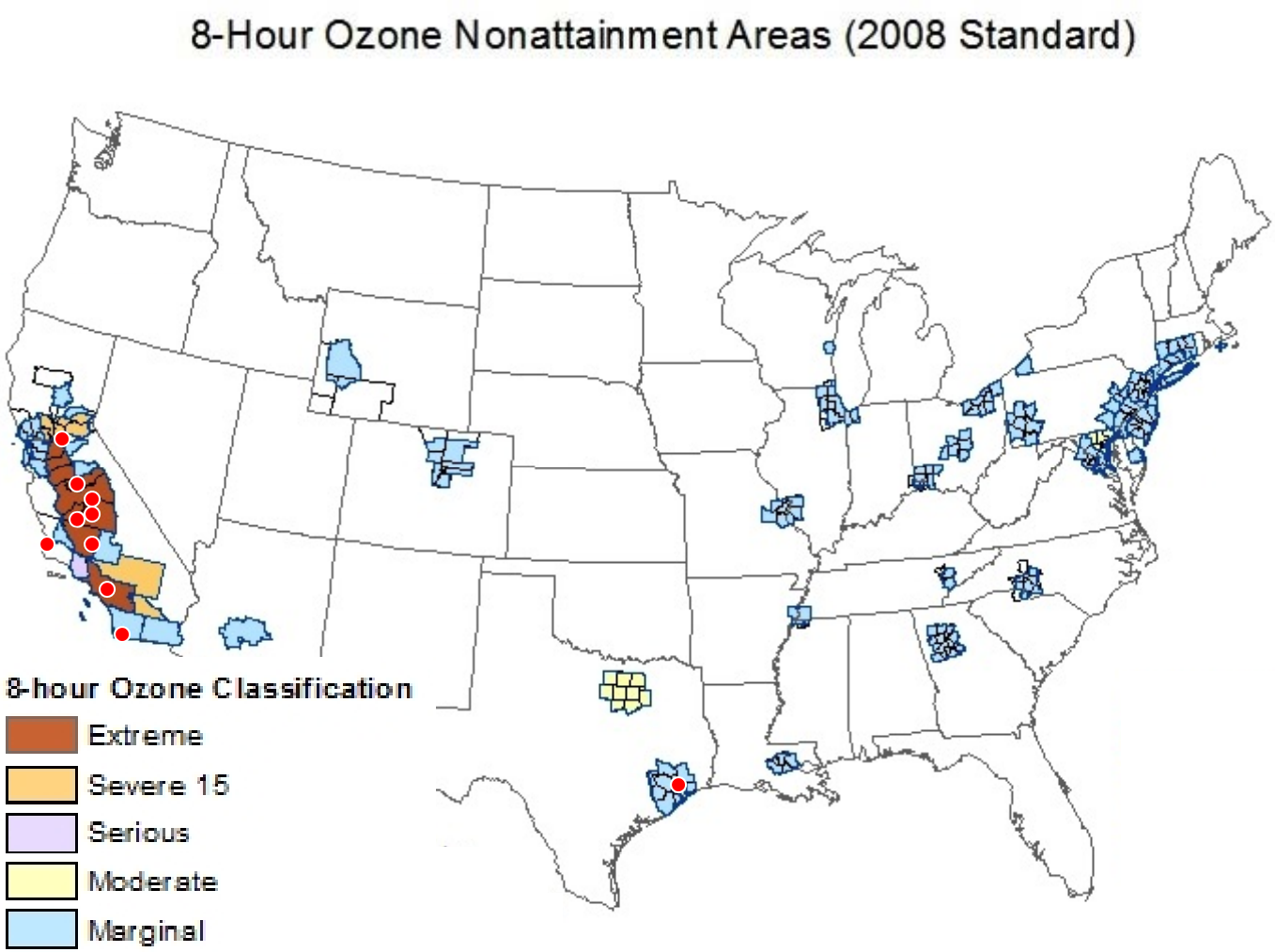


Worst Cities ($PM_{2.5}$)

1) Bakersfield, CA
2) Fresno, CA
3) Hanford, CA
4) Los Angeles, CA
5) Modesto, CA
6) Pittsburgh, PA
7) Salt Lake City, UT
8) Logan, UT
9) Fairbanks, AK
10) Merced, CA

U.S. EPA & American Lung Assoc. (2012)

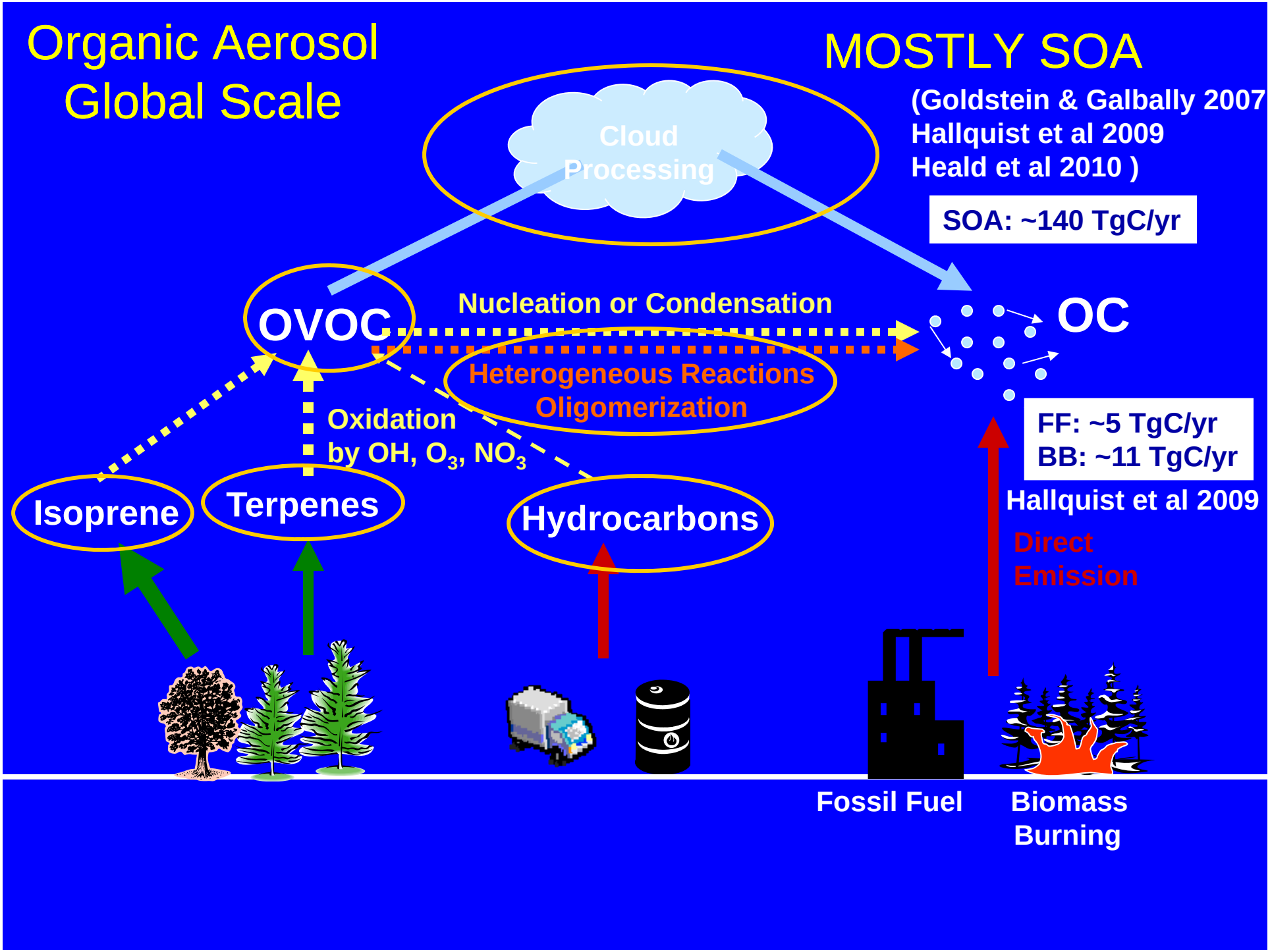
Ozone Nonattainment Areas in U.S.



Worst Cities (O_3)

1) Los Angeles, CA
2) Visalia, CA
3) Bakersfield, CA
4) Fresno, CA
5) Hanford, CA
6) Sacramento, CA
7) San Diego, CA
8) Houston, TX
9) San Luis Obispo, CA
10) Merced, CA

U.S. EPA & American Lung Assoc. (2012)


Organic Aerosol
Global Scale
MOSTLY SOA
(Goldstein & Galbally 2007
Hallquist et al 2009
Heald et al 2010)
SOA: ~140 TgC/yr
Cloud
Processing
OVOC
Nucleation or Condensation
OC
Heterogeneous Reactions
Oligomerization
Oxidation
by OH, O_3, NO_3
FF: ~5 TgC/yr
BB: ~11 TgC/yr
Hallquist et al 2009
Isoprene
Terpenes
Hydrocarbons
Direct
Emission
Fossil Fuel
Biomass
Burning

Anthropogenic Versus Biogenic Volatile Organic Compounds

AVOC ~100 Tg C/yr

Mobile Sources

Fossil Fuel (power plants)

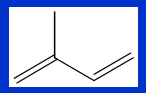
Fire

Solvents/Paints

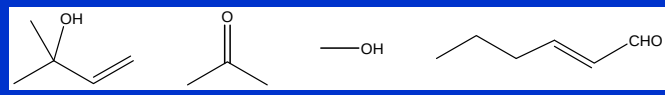
Etc.

BVOC ~1150 Tg C/yr

Isoprene (500)

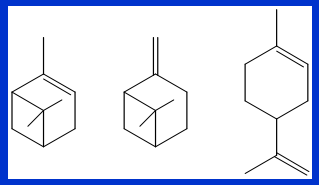


Other VOC (260)

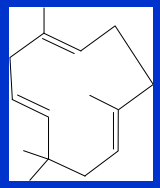


Other Reactive VOC (260)

Monoterpenes (130)



Sesquiterpenes (?)



Globally BVOC = 10 X AVOC
In California, relative contribution of AVOC and BVOC is poorly constrained, and varies significantly among air districts.

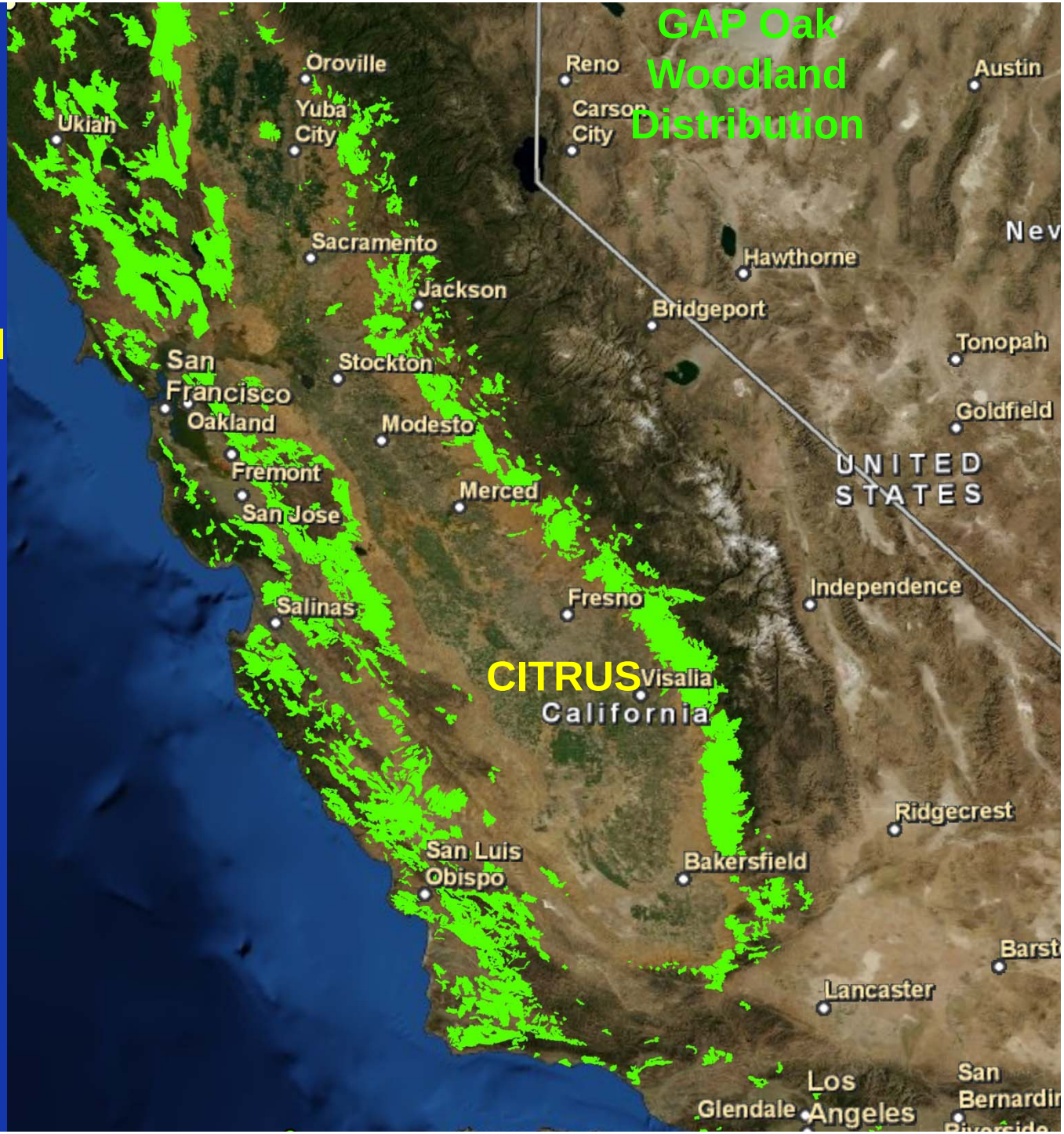
Guenther et al 1995

Motivation

- Vegetation in California comprises a large source of BVOC, which react with anthropogenic pollutants and contribute to photochemical ozone and particle formation.
- In many regions, Isoprene is the most important VOC affecting regional air quality, and the vast majority of isoprene emissions are expected to occur from oak trees which cover ~7% of CA land surface.
- Previous BVOC emission measurements from CA oaks were made almost exclusively at branch and leaf levels (e.g. Winer et al., 1992).
- BVOC emission measurements are needed at the landscape scale in CA to evaluate and improve BVOC emission models used for air quality State Implementation Plan (SIP) development.

3 Recent CARB Funded Field Campaigns Provide new insight on BVOC Emissions

1) CITRUS Agricultural Crop Emissions (valley floor)

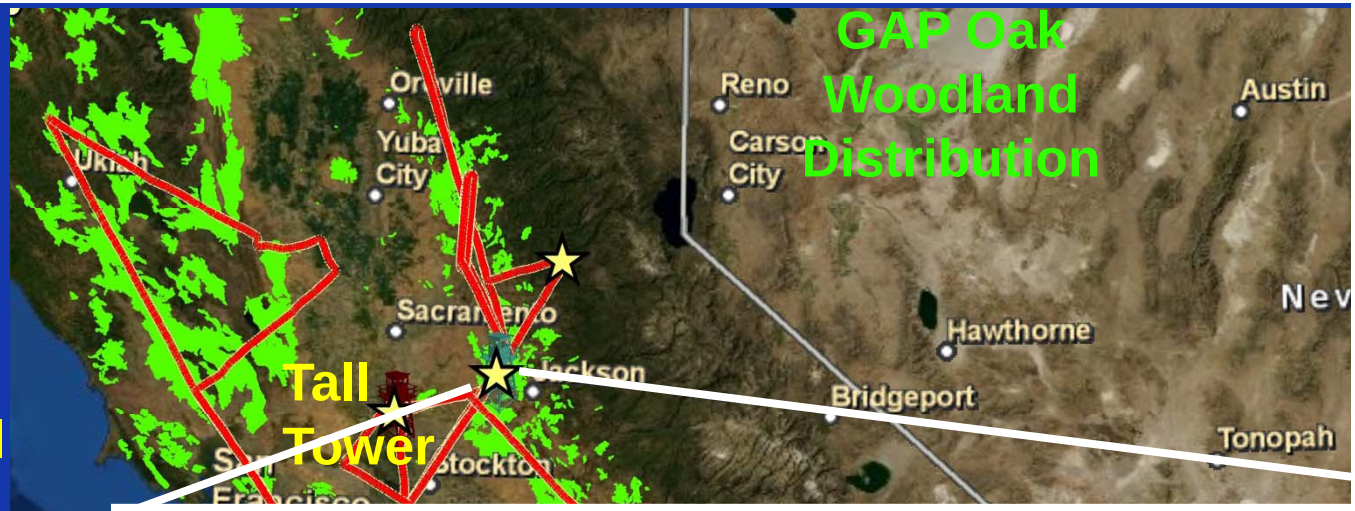


3 Recent CARB Funded Field Campaigns Provide new insight on BVOC Emissions

1) CITRUS Agricultural Crop Emissions (valley floor)

2) CABERNET Aircraft Flux Study (Flight Tracks in Red)

3) TALL TOWER Walnut Grove (525 m) vertical profiles (integrate over large area of Central Valley)



CABERNET (June 2011)

California Airborne BVOC Emission Research in Natural Ecosystem Transects

Karl et al JAS, 2013

Misztal et al ACP, 2014

Misztal et al 2015 in review

California Environmental Protection Agency AIR RESOURCES BOARD

NOAA

Berkeley University of California

NCAR

NPS PRAESTANTIA PER SCIENTIAM

CABERNET Objectives

- Evaluate airborne VOC flux methods on regional scale
- Investigate the vertical transport of isoprene in the planetary boundary layer (PBL)
- Characterize landcover effects on isoprene emissions
- Verify and improve isoprene emission models

Flight track planning

Flight planning criteria

1) Isoprene Emission Model Discrepancies:

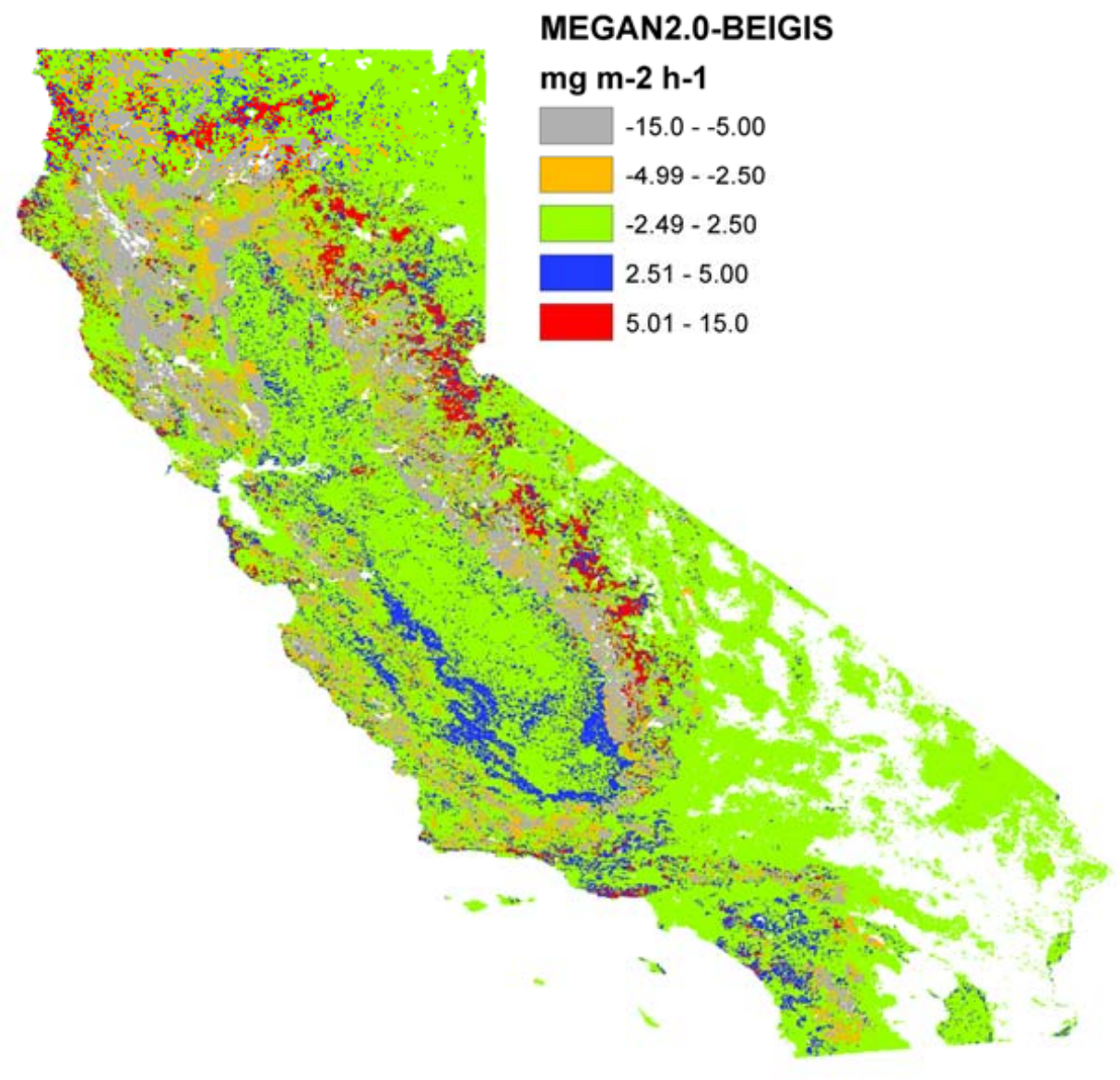
a) BEIGIS>>MEGAN (grey)

b) BEIGIS<<MEGAN (red)

c) BEIGIS<MEGAN (blue)

2) Relatively flat terrain

3) Expected high emission regions (location of oaks)

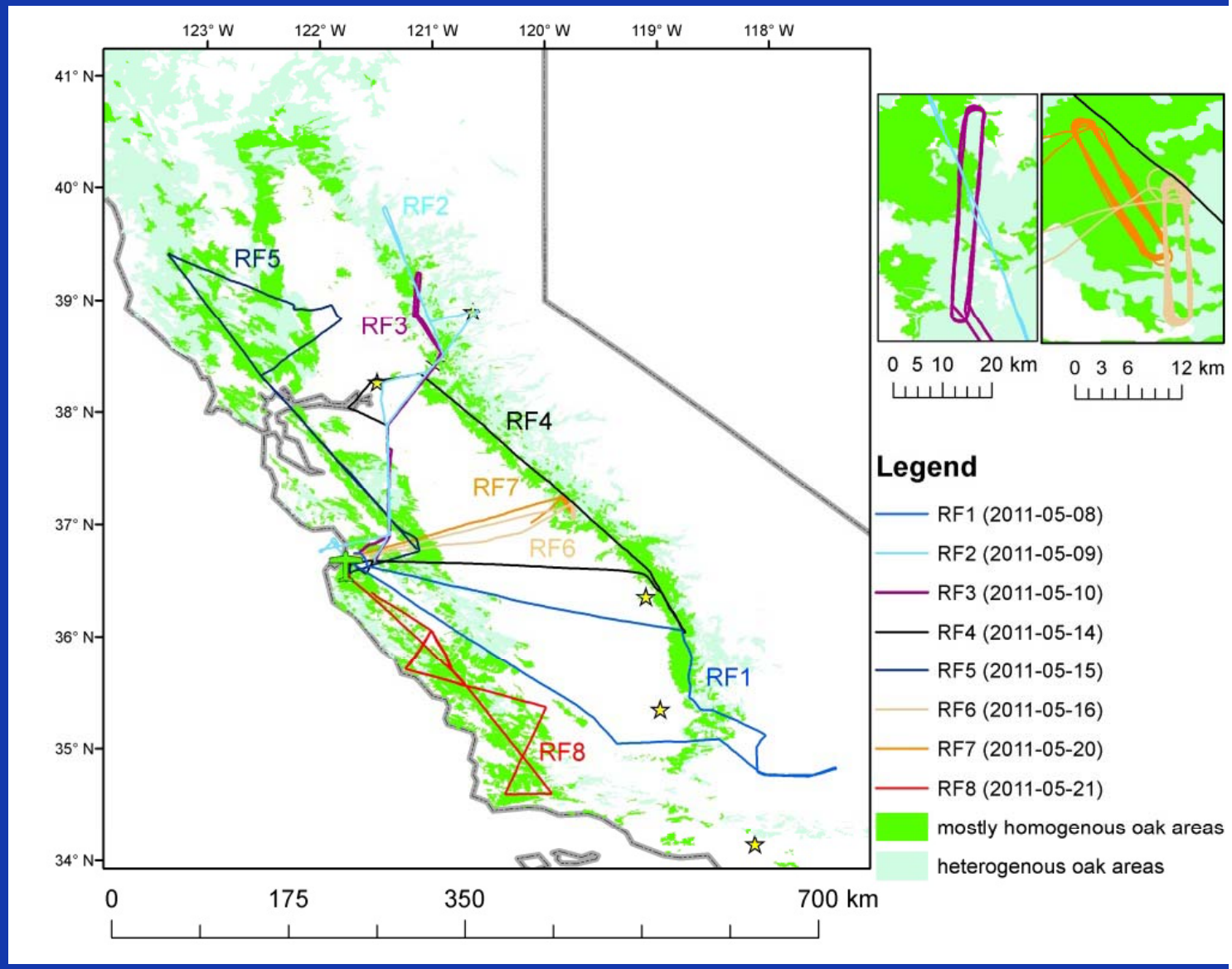


Research Flight's & Oak Distribution

<u>8 Research Flights</u>
40 hrs, ~10,000 km
mostly at 400±50m

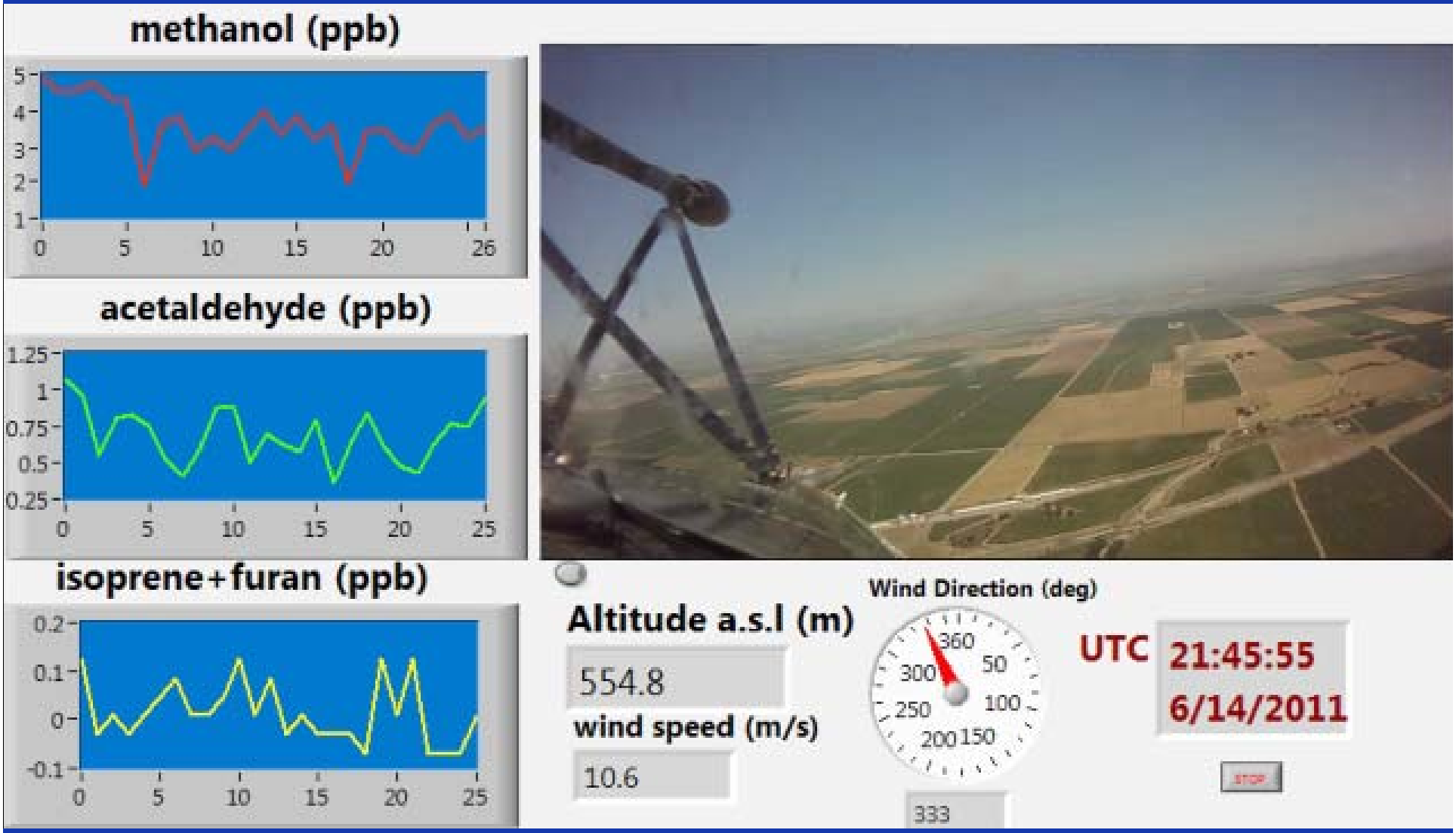
<u>Payload</u>
VOCs by PTRMS
Isoprene,
MVK+MACR,
Methanol,
Monoterpenes,
occasional other species

CH_4 (Picarro)
CO_2 (Picarro)
O_3 (fast&slow (2B))
3D Winds
Micrometeorology
Radiation



Ready for RF1….

We can fly again on the camera and see how the chemistry changed in different places



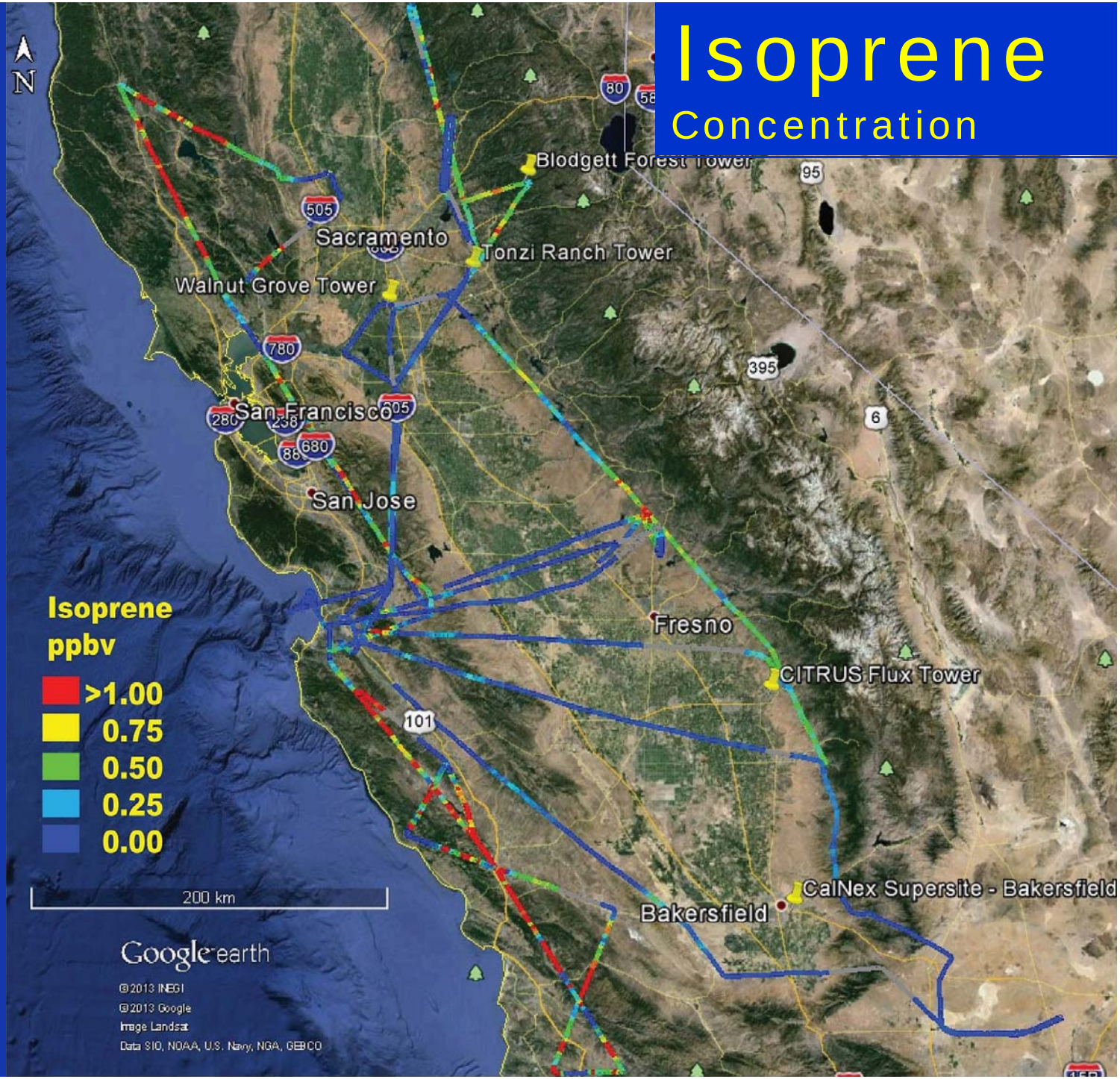
Isoprene
Concentration

All Flights at Midday ~10am-4pm

NOTICE: Higher concentration over hills surrounding valley - oak woodlands.

Lower over valley - agriculture.

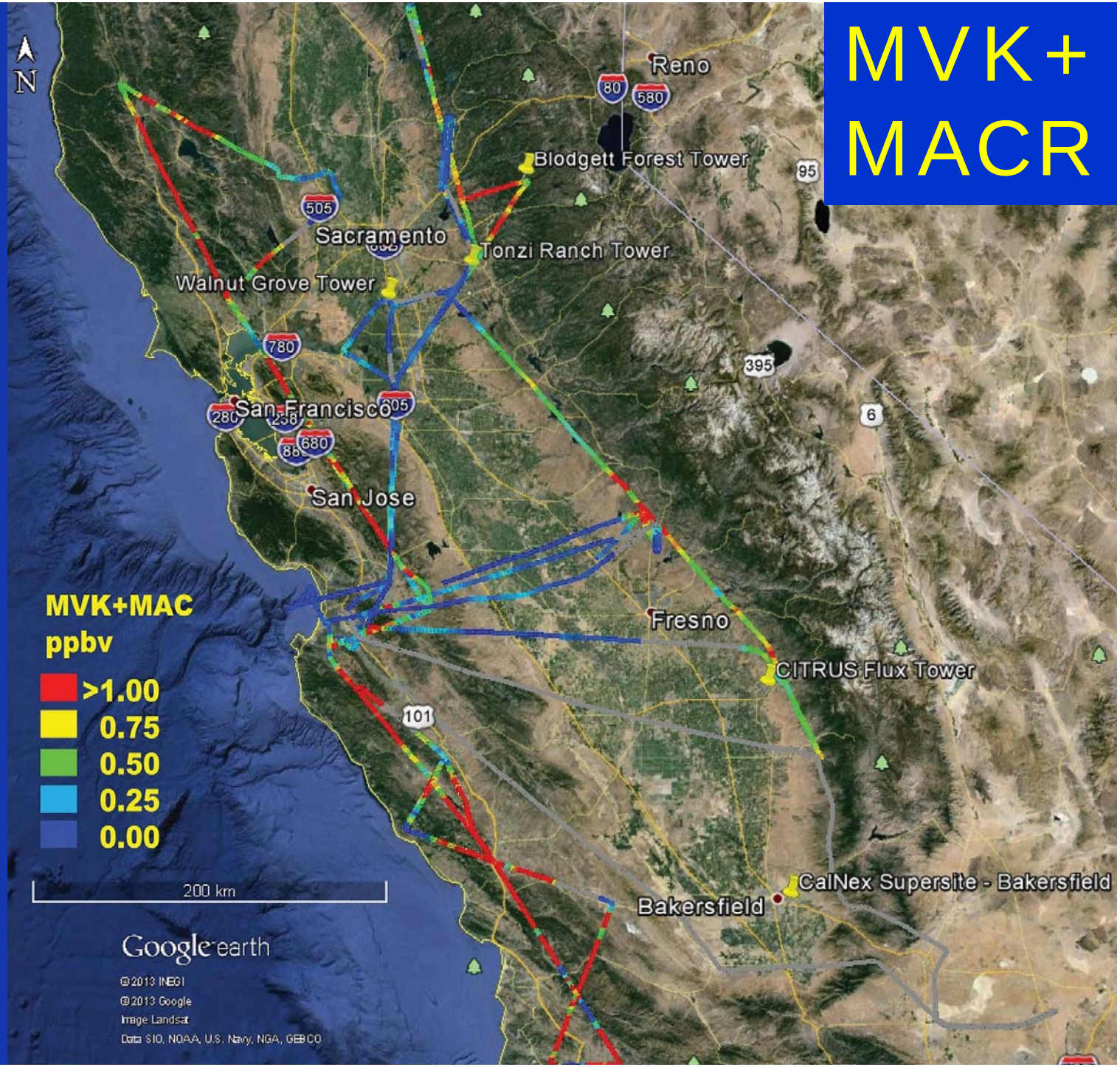
Misztal et al. 2014



High MVK+MACR over hills & mountains, low over valley.

Ratio of *<u>isoprene</u>* *(MVK+MACR)* decreased downwind of sources and with increasing altitude

Misztal et al. 2014

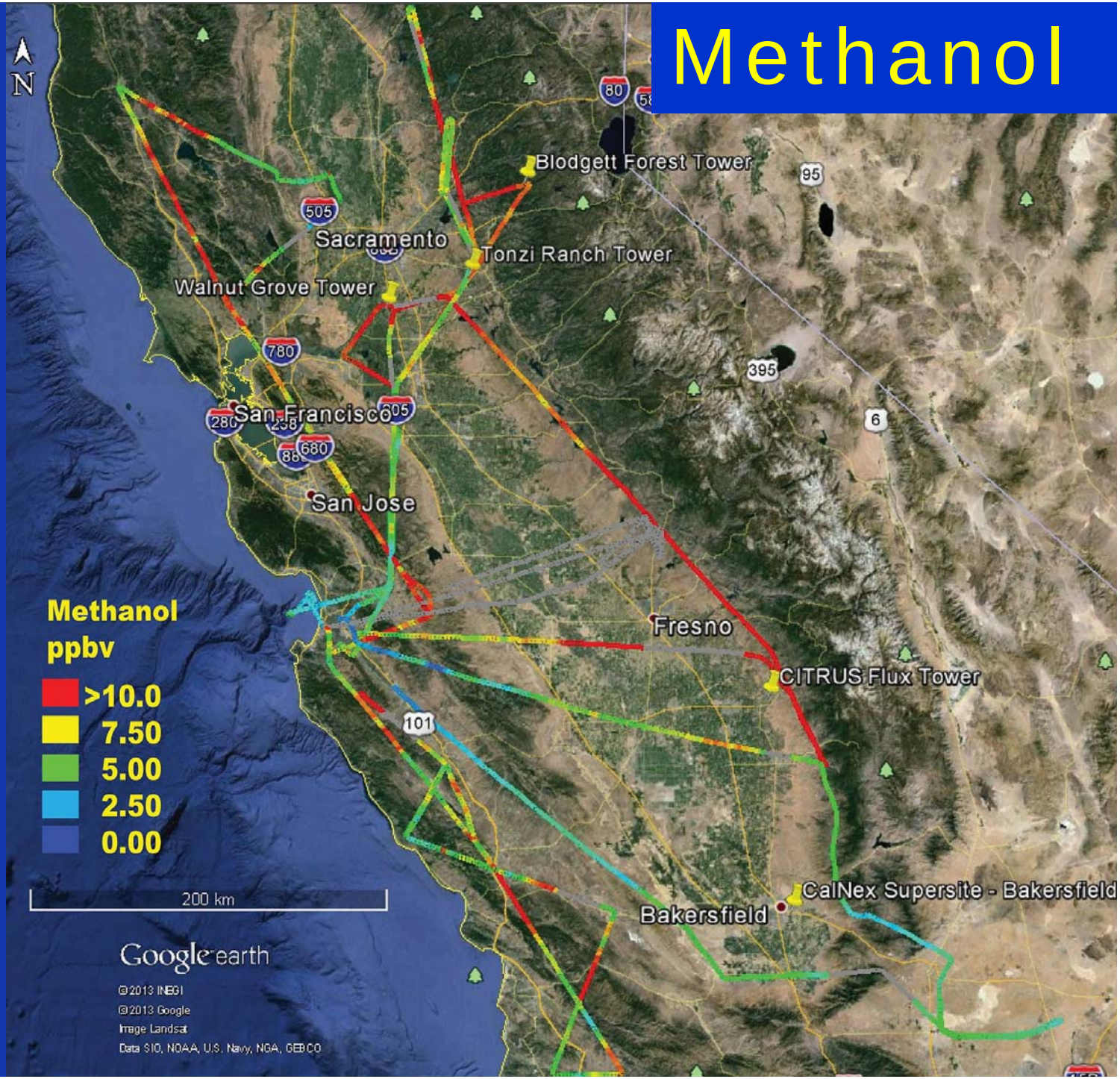


Methanol

High over hills and mountains, and some high levels over valley.

Large increases observed above and downwind of dairies (coincident increases in methane).

Misztal et al. 2014

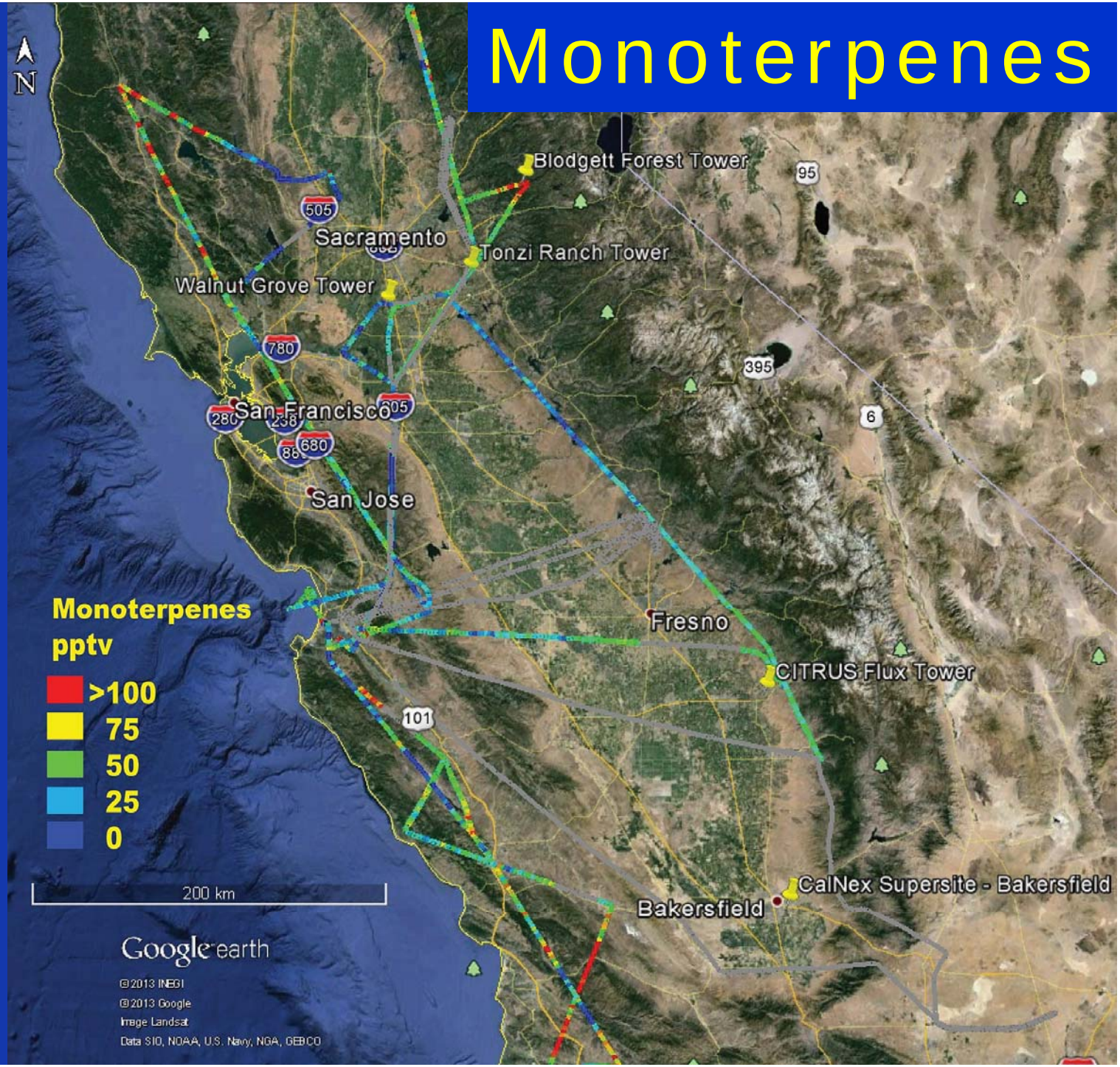


Monoterpenes

High over coniferous regions (Blodgett, N and S Coast Ranges)

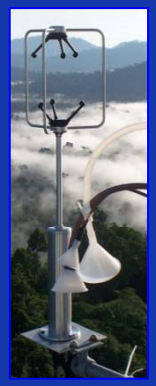
Low over oaks in the foothills.

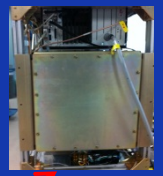
Very reactive and low abundance - challenging to measure at aircraft altitudes



Misztal et al. 2014

Airborne Eddy Covariance

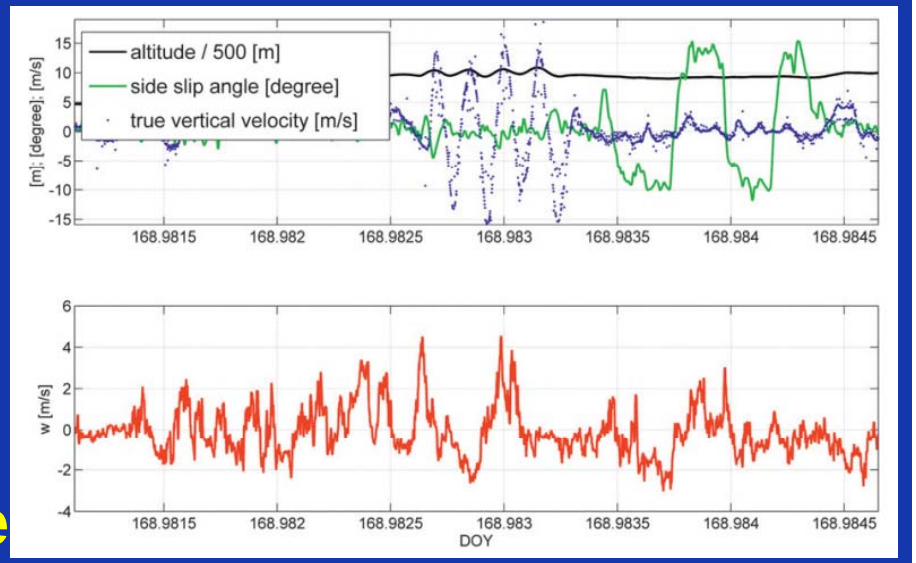




Ground

Airborne

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



Lenschow maneuvers are applied to minimize effects of aircraft movement on vertical wind velocity Karl et al. (2013)

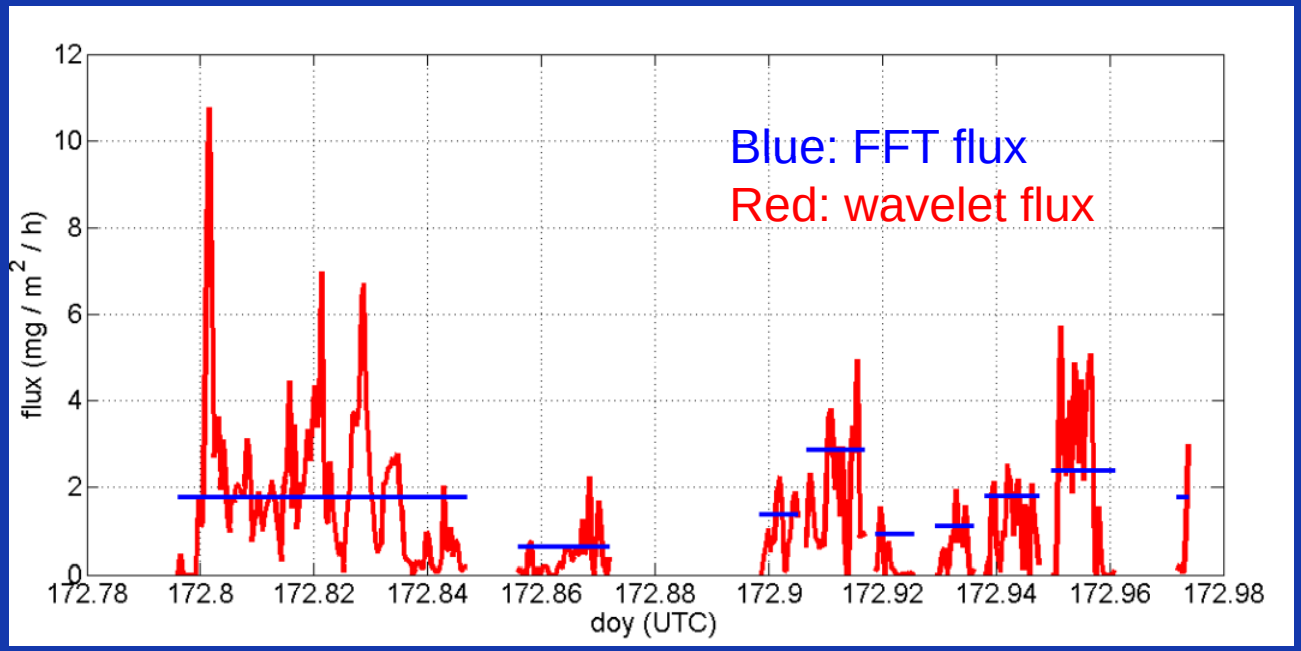
General Rule: "FLY LOW AND SLOW"

Lenschow et al. (1994) , Desjardins et al. (1989) , Karl et al. (2009, 2013), Misztal et al. (2014)

Airborne Eddy Covariance

1. **Fast Fourier Transform (FFT) – classic, 1 value per transect (e.g. 100 km)**

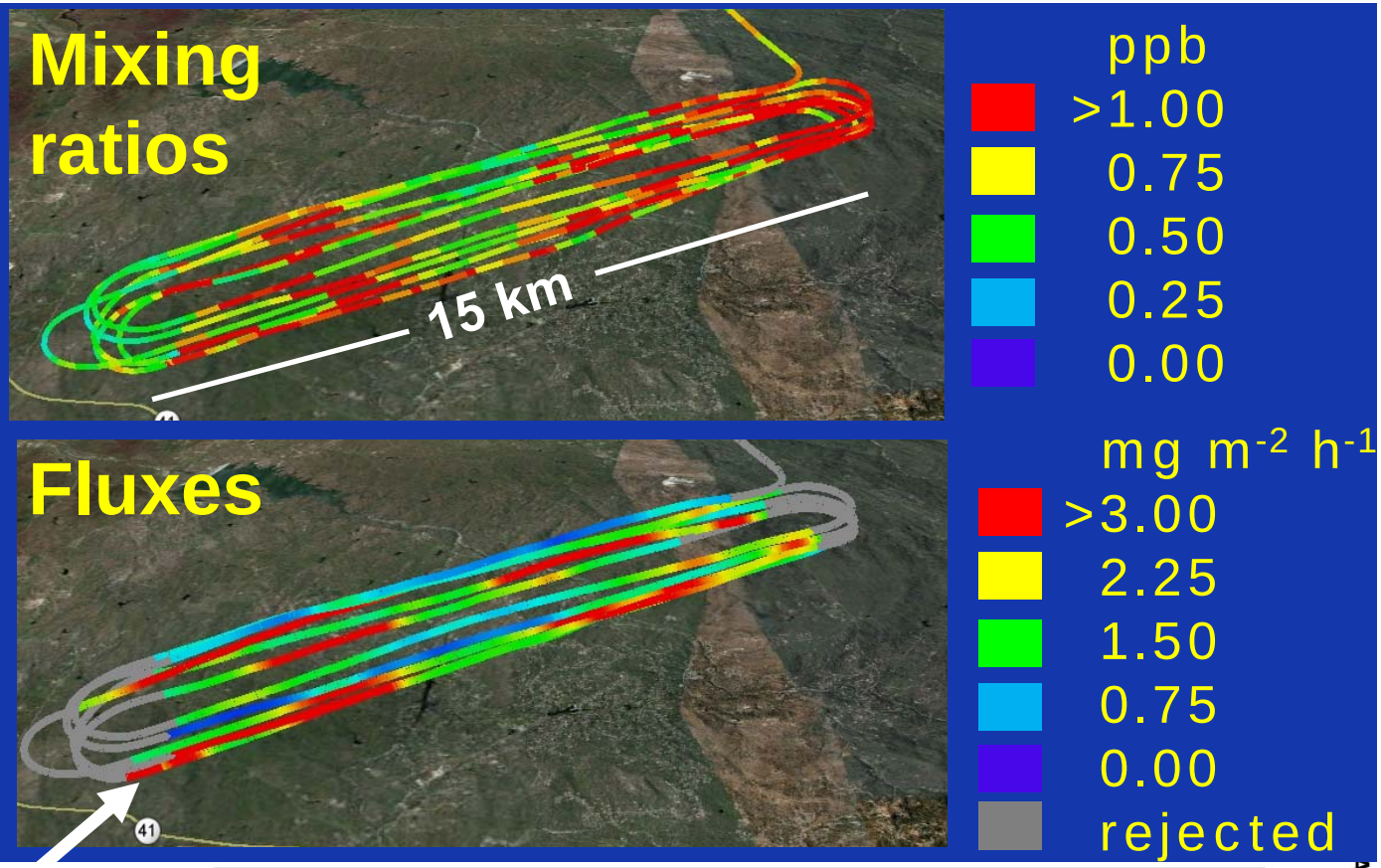
2. **Continuous Wavelet Transformation (CWT) – new method, high spatiotemporal resolution**



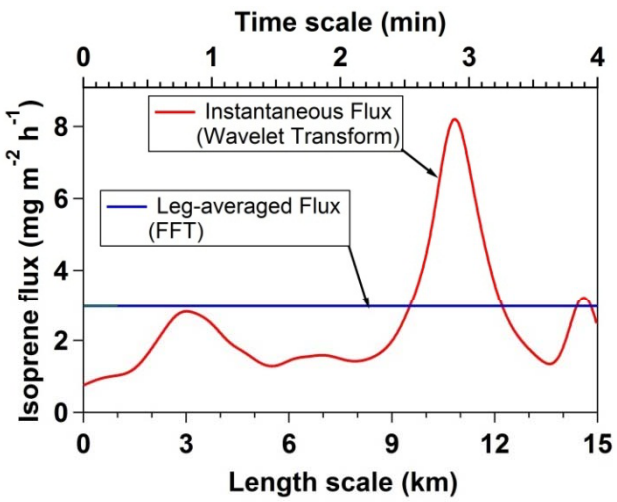
Karl et al. 2013, Misztal et al. 2014

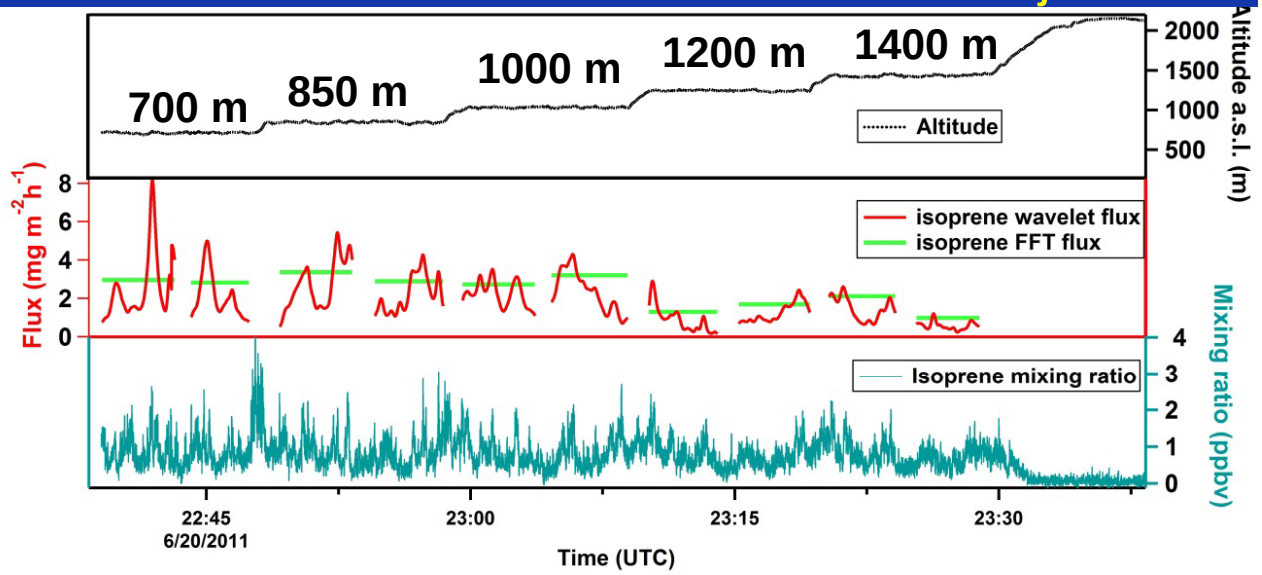
“Racetracks” show vertical gradients in isoprene flux over oak woodlands

Karl et al., JAS 2013

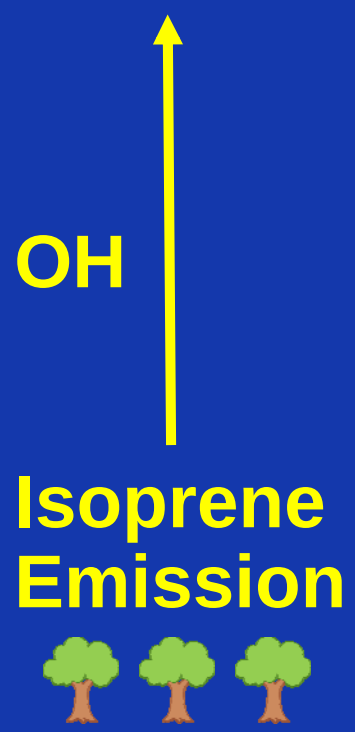


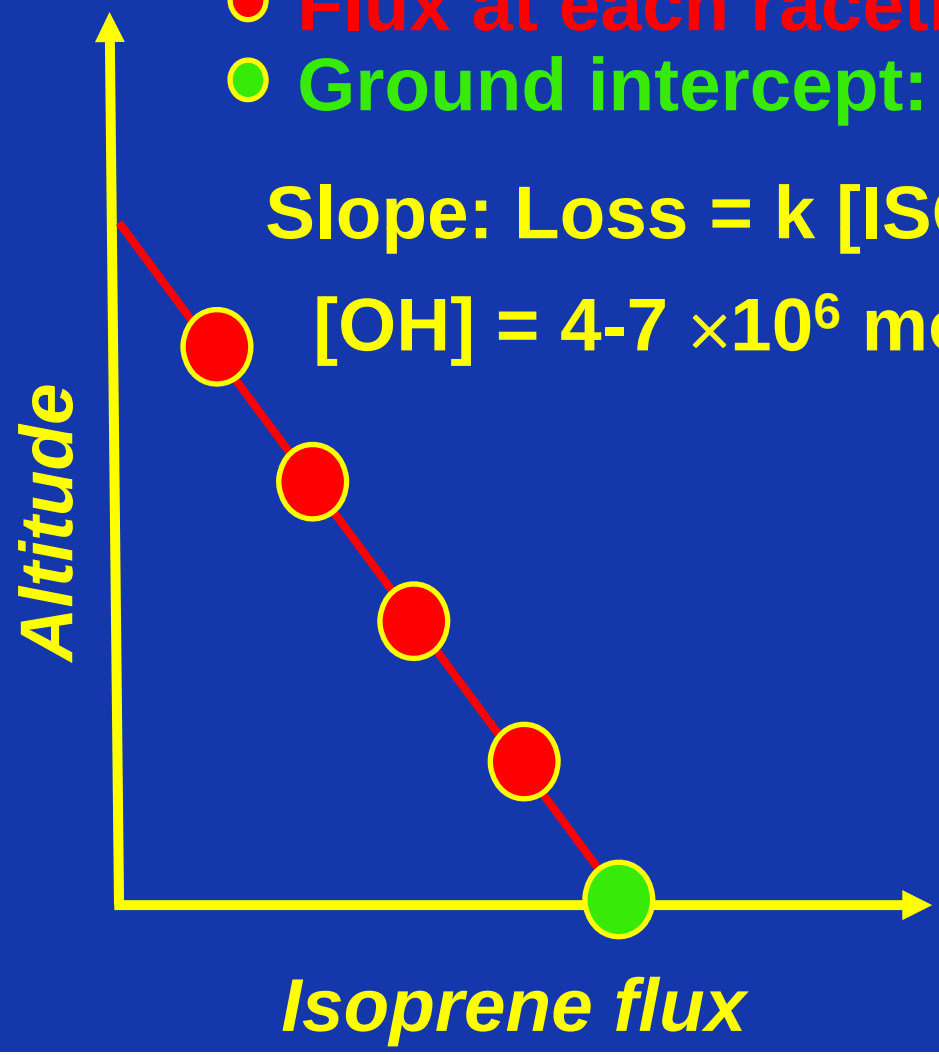
Flux at lowest level





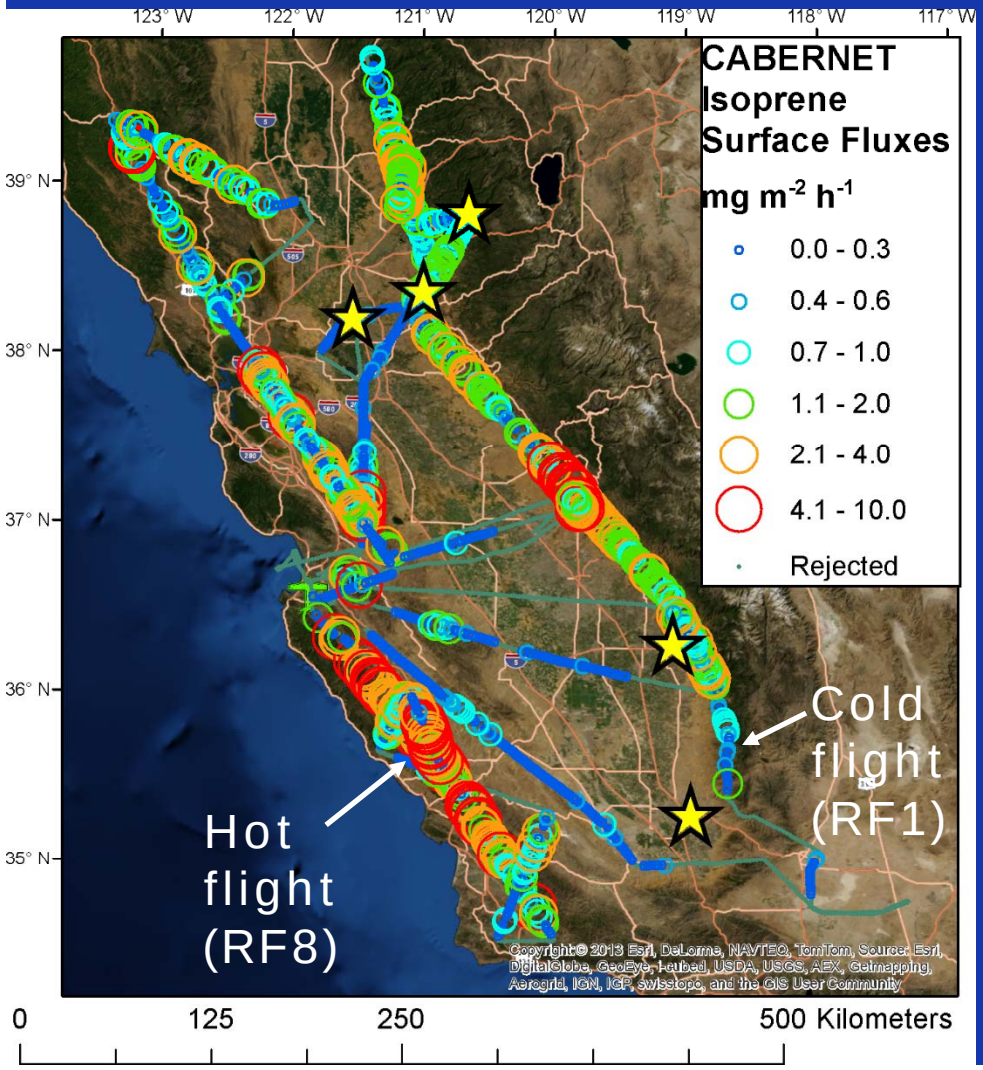
Flux divergence measurement used to determine OH and surface flux





Measured Isoprene Surface Fluxes and Basal Emission Rates (BERs)

(similar spatial pattern as concentration)



Isoprene emission (Flux) from plants exhibits exponential sensitivity to temperature and PAR and the emission capacities are also linked to previous history of meteorological conditions (Guenther et al., 2006)

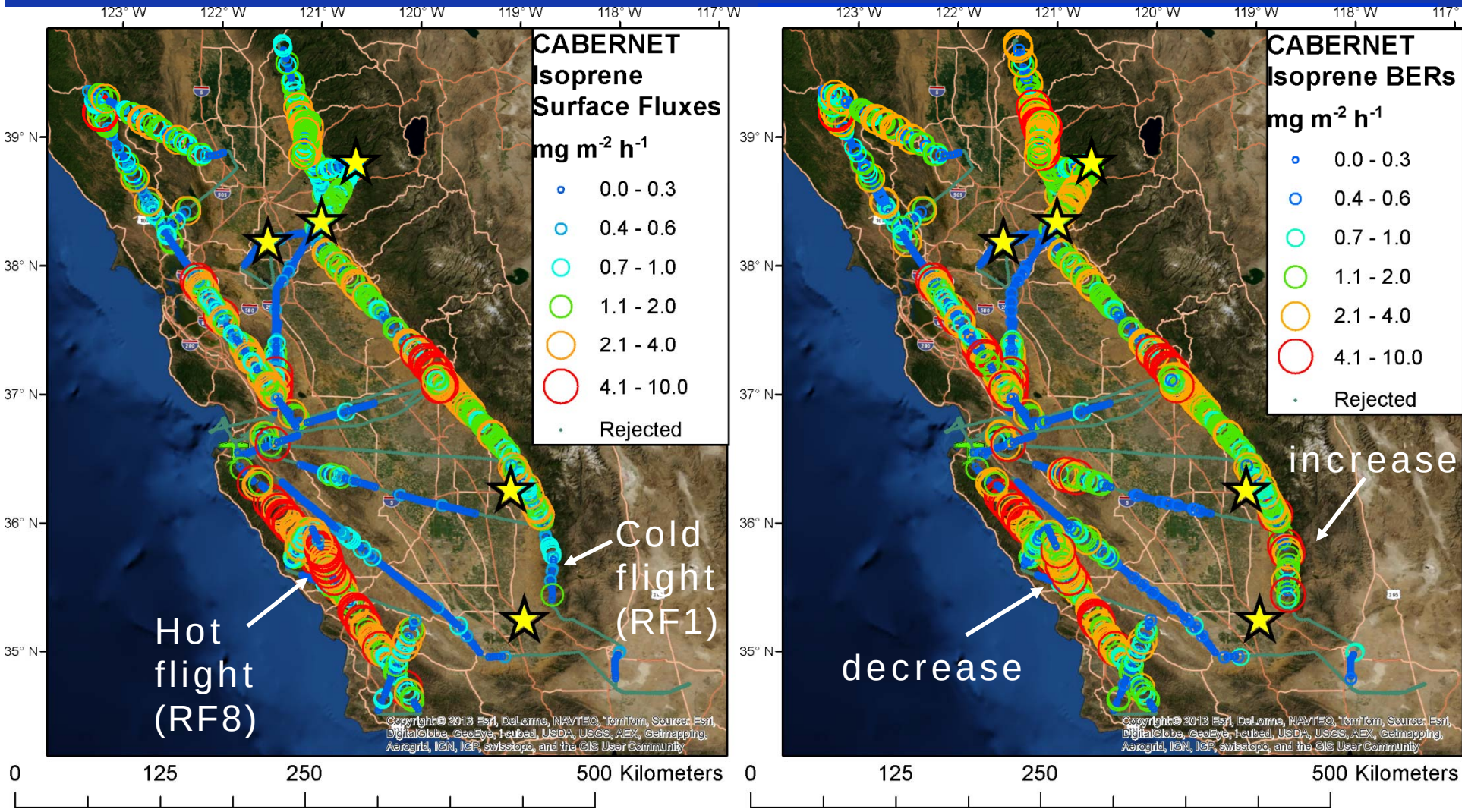
$$F = BER \times \gamma_T \times \gamma_{PAR}$$

Measured at standard conditions 30 °C, 1000 μmol m^{-2} s^{-1} PAR

$$BER = \frac{F_{\text{airborne}}}{\gamma_T \times \gamma_{PAR}}$$

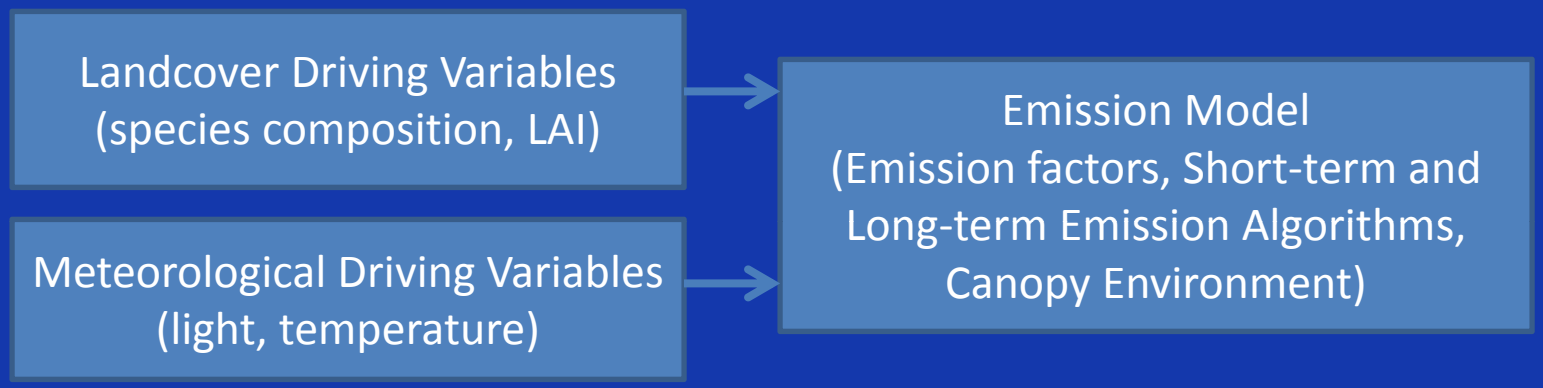
Measured Isoprene Surface Fluxes and Basal Emission Rates (BERs)

(similar spatial pattern as concentration)



Using Aircraft Isoprene Flux to verify and improve emission models

- Examine 2km resolution flux data
- Test the models, and the model inputs



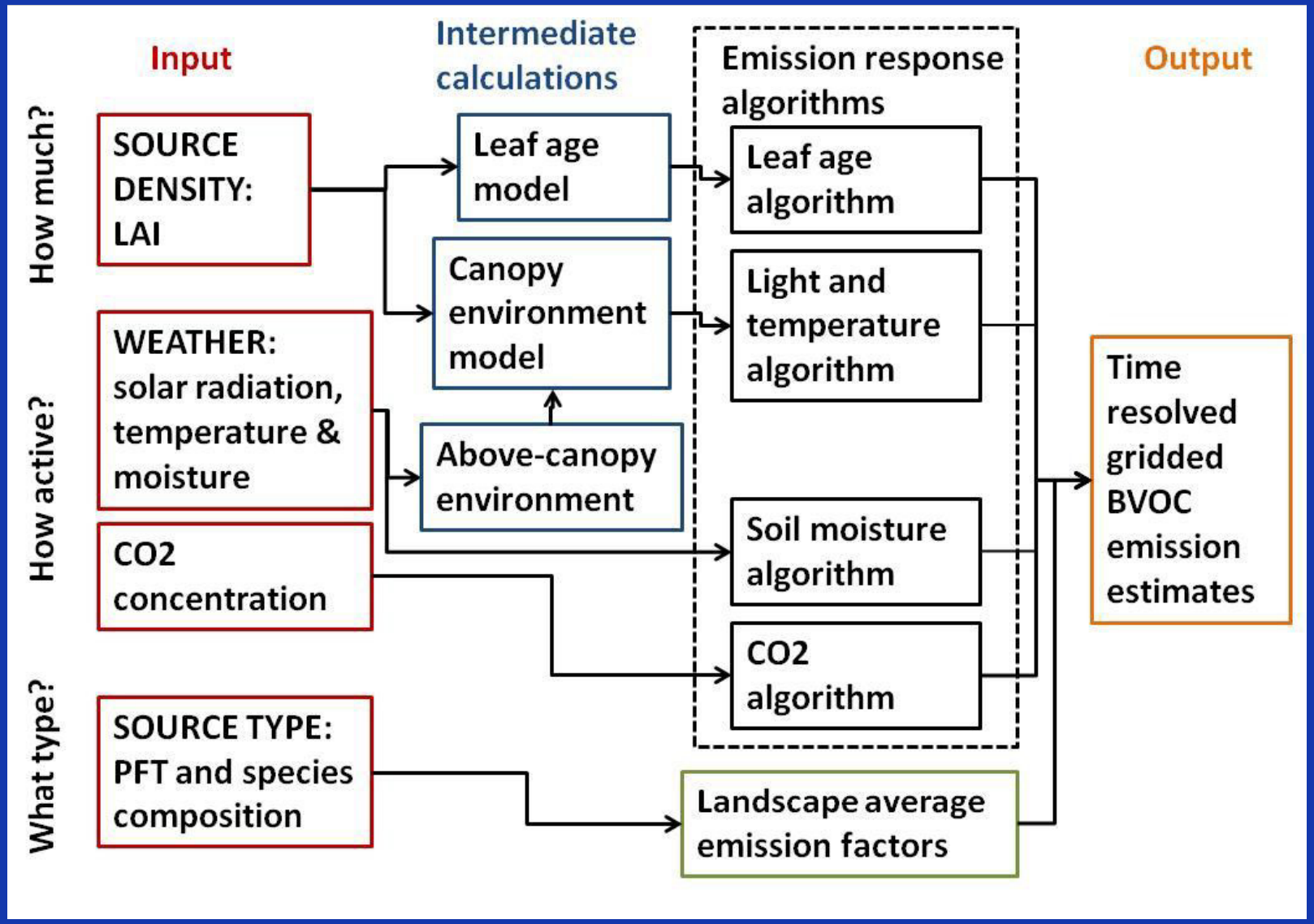
- Most Uncertain Input? Landscape weighted emission factor datasets

  -based on species composition and species-specific emission factors

  - **BEIGIS** (California ARB Model) - GAP landcover database for oaks, with Forest Inventor Analysis (FIA, USFS product)
  - **MEGAN 2.0**, landcover 2.1 (Guenther et al. 2006) – WestGAP/FIA
  - **MEGAN 2.1**, landcover 2.2 (Guenther et al. 2012) - NLCD/FIA/PFT

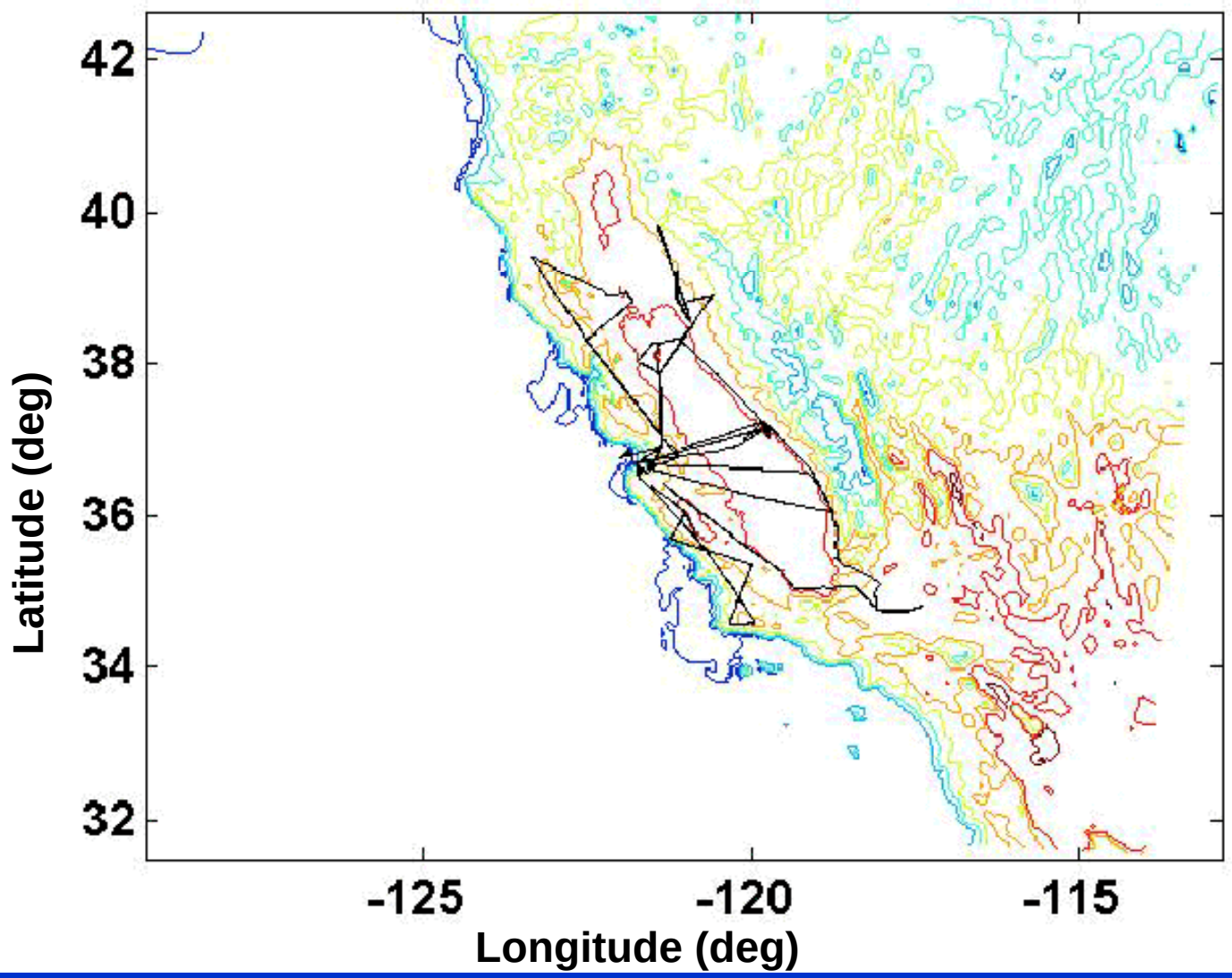
Lots of other options for models with different landcover:
BELD (BEIS, Pierce et al. 1991), BELD2 (BEIS2, Geron et al. 1994), BELD3 (BEIS3, Kinnee et al. 1997), GED (GEIA inventory, Guenther et al. 1995)

MEGAN model components and driving variables

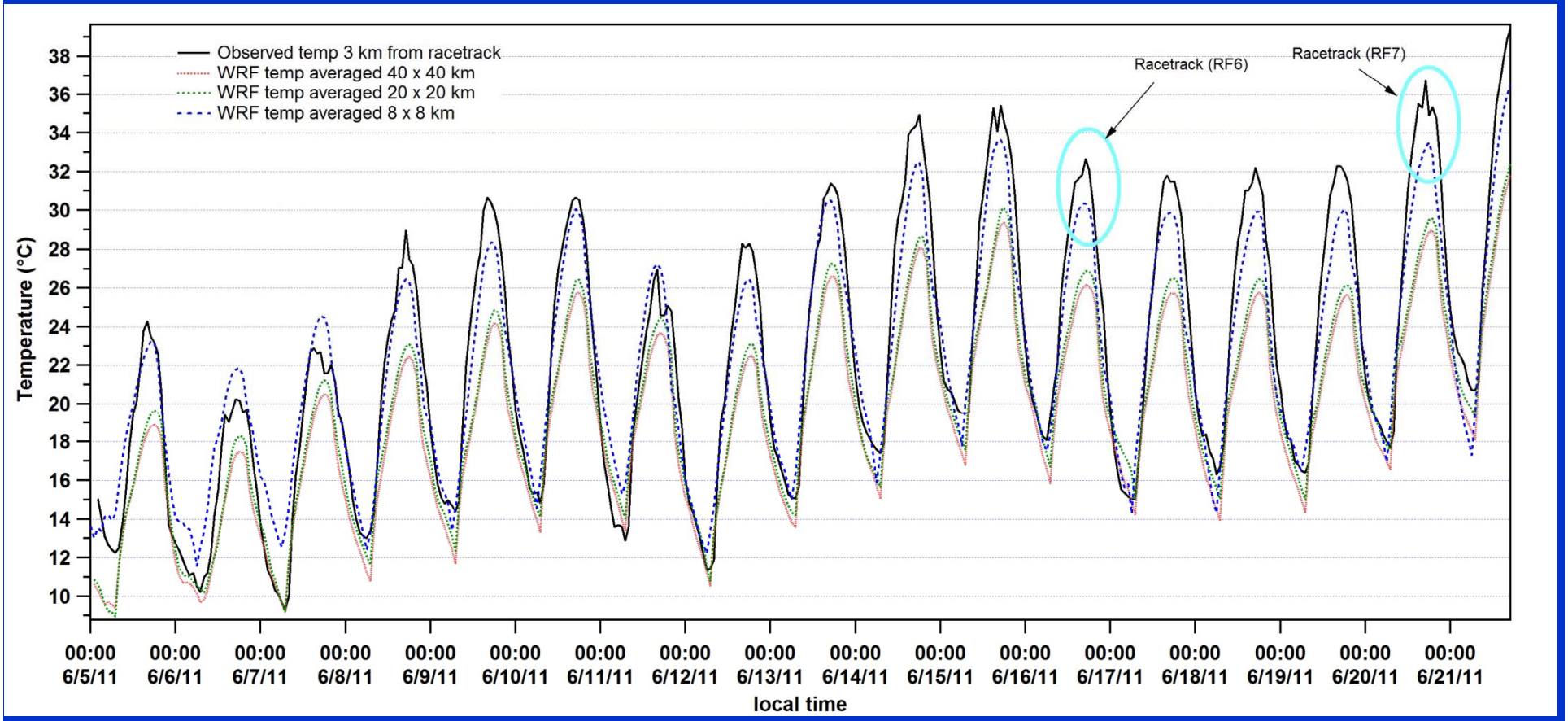


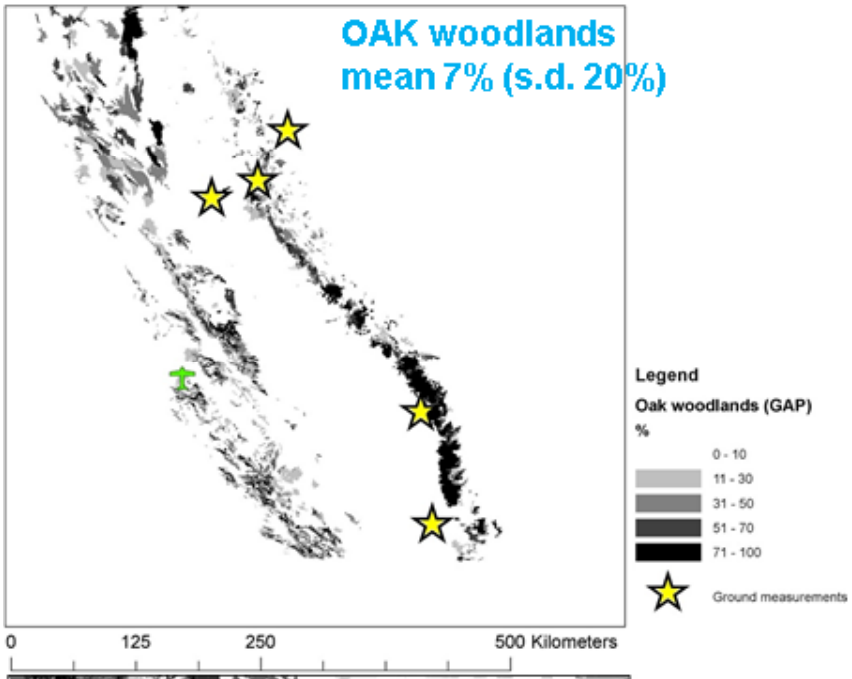
(Guenther et al. 2012)

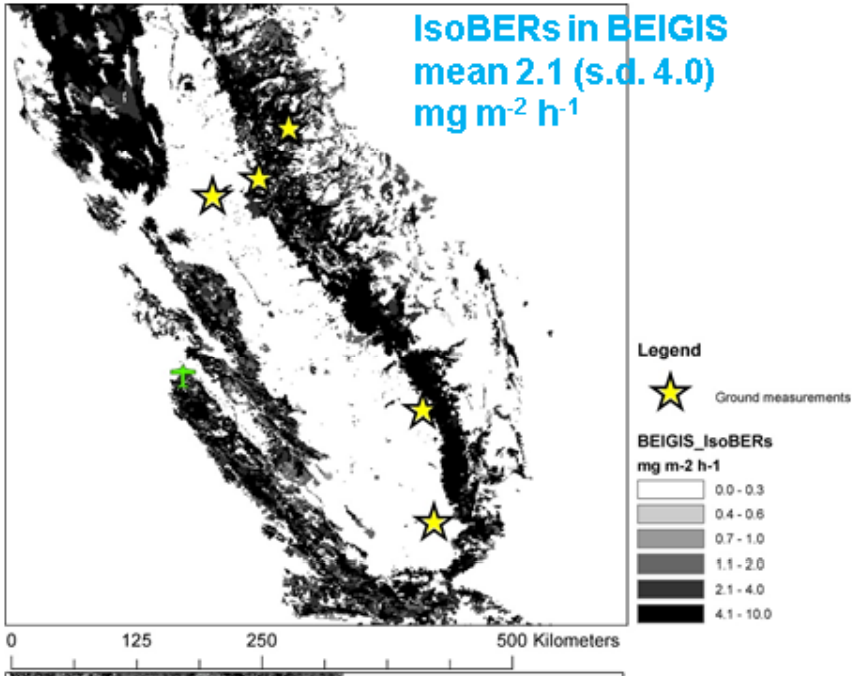
WRF temperature has large gradients (used to drive BVOC emission models)

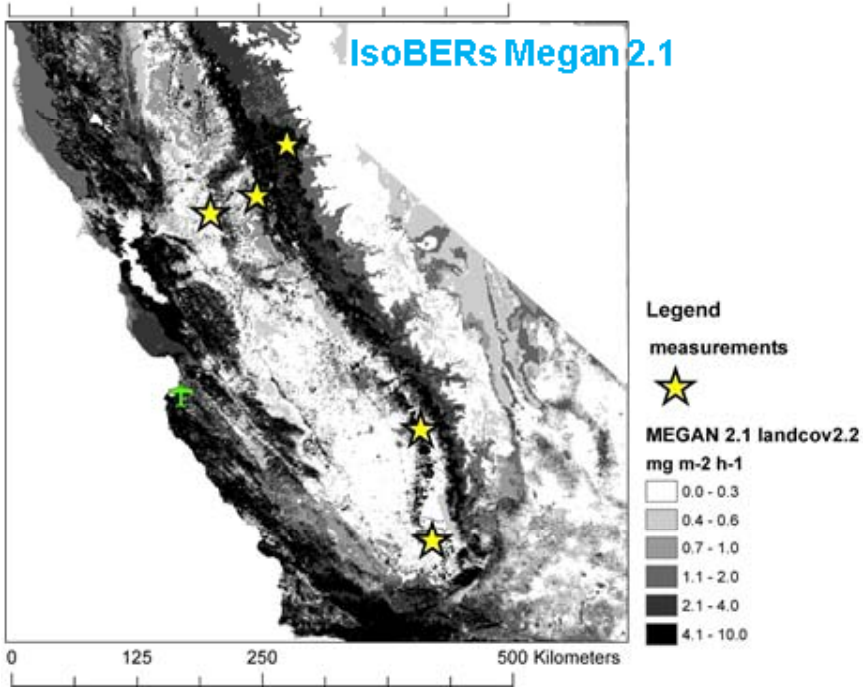


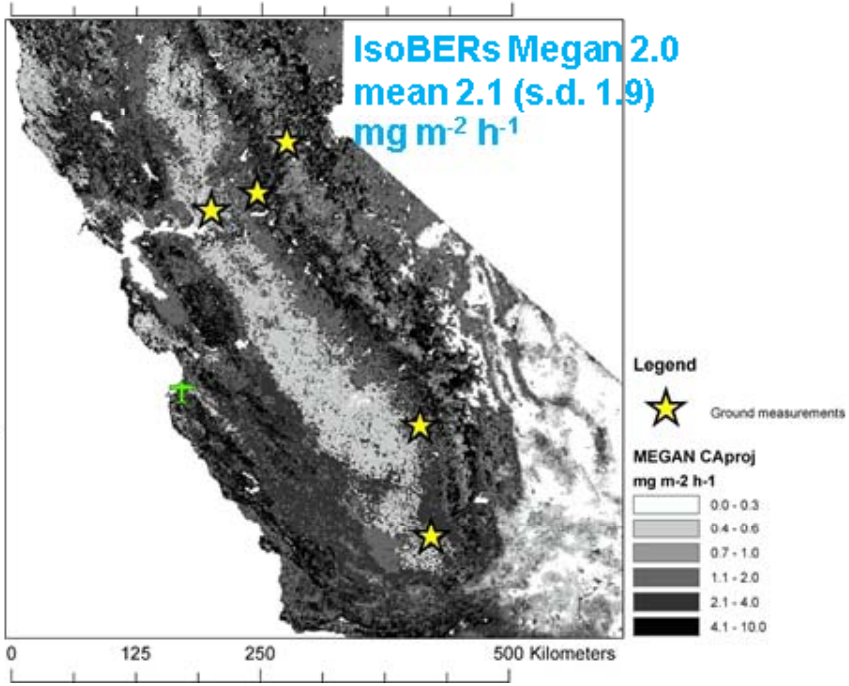
WRF temperature resolution is critical in particular in the foothills

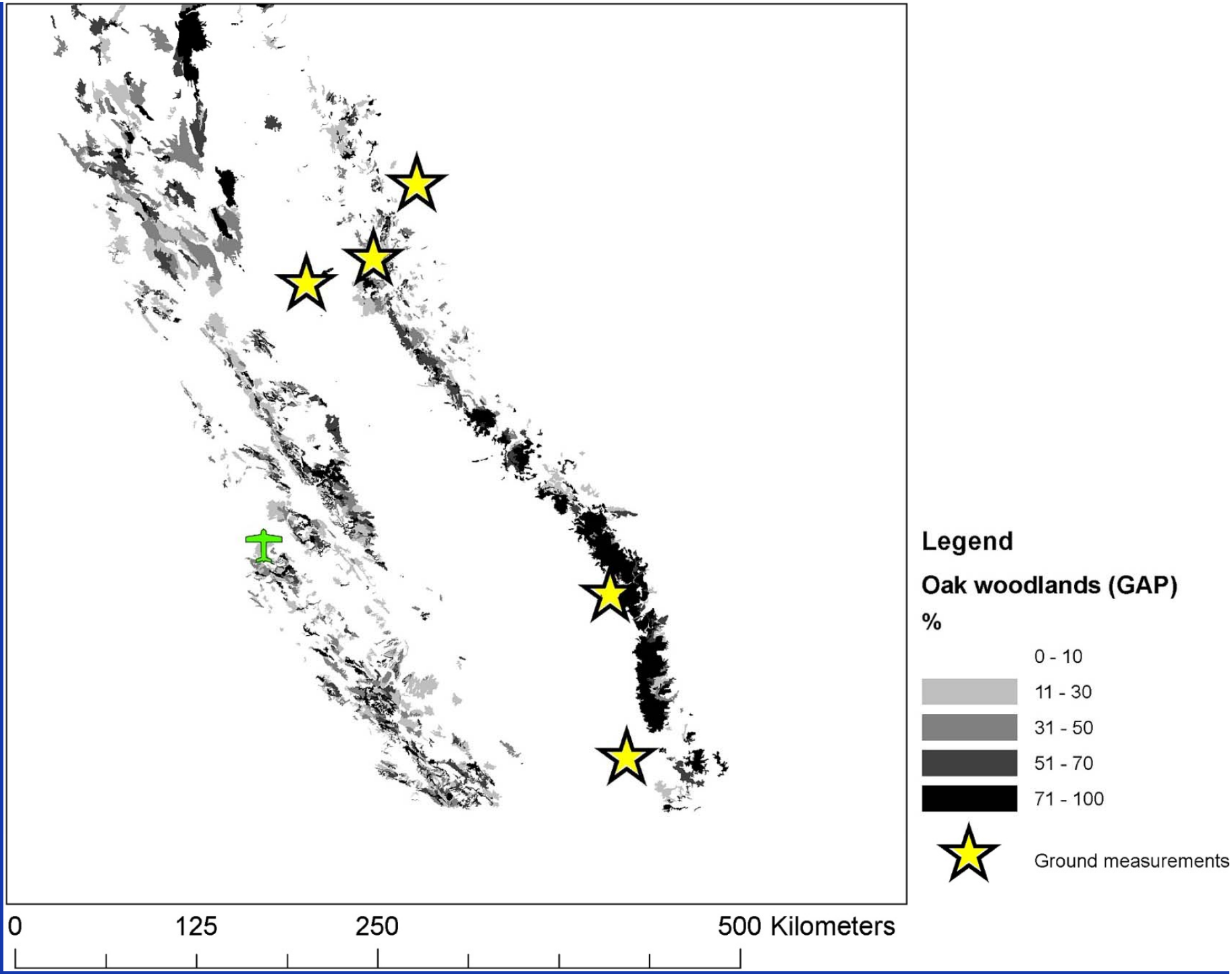


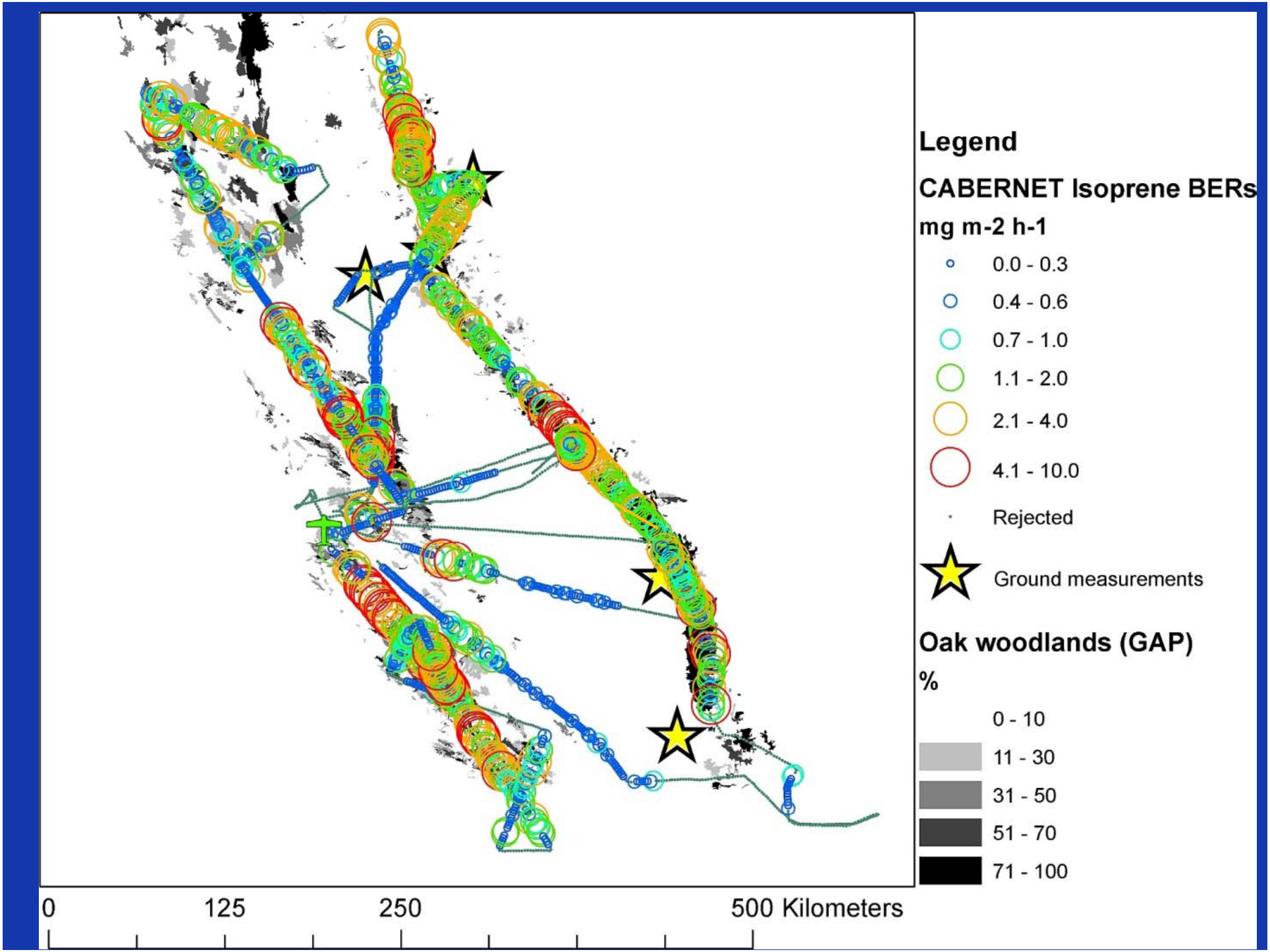

OAK woodlands
mean 7% (s.d. 20%)
Legend
Oak woodlands (GAP)
%
0 - 10
11 - 30
31 - 50
51 - 70
71 - 100
Ground measurements
0
125
250
500 Kilometers

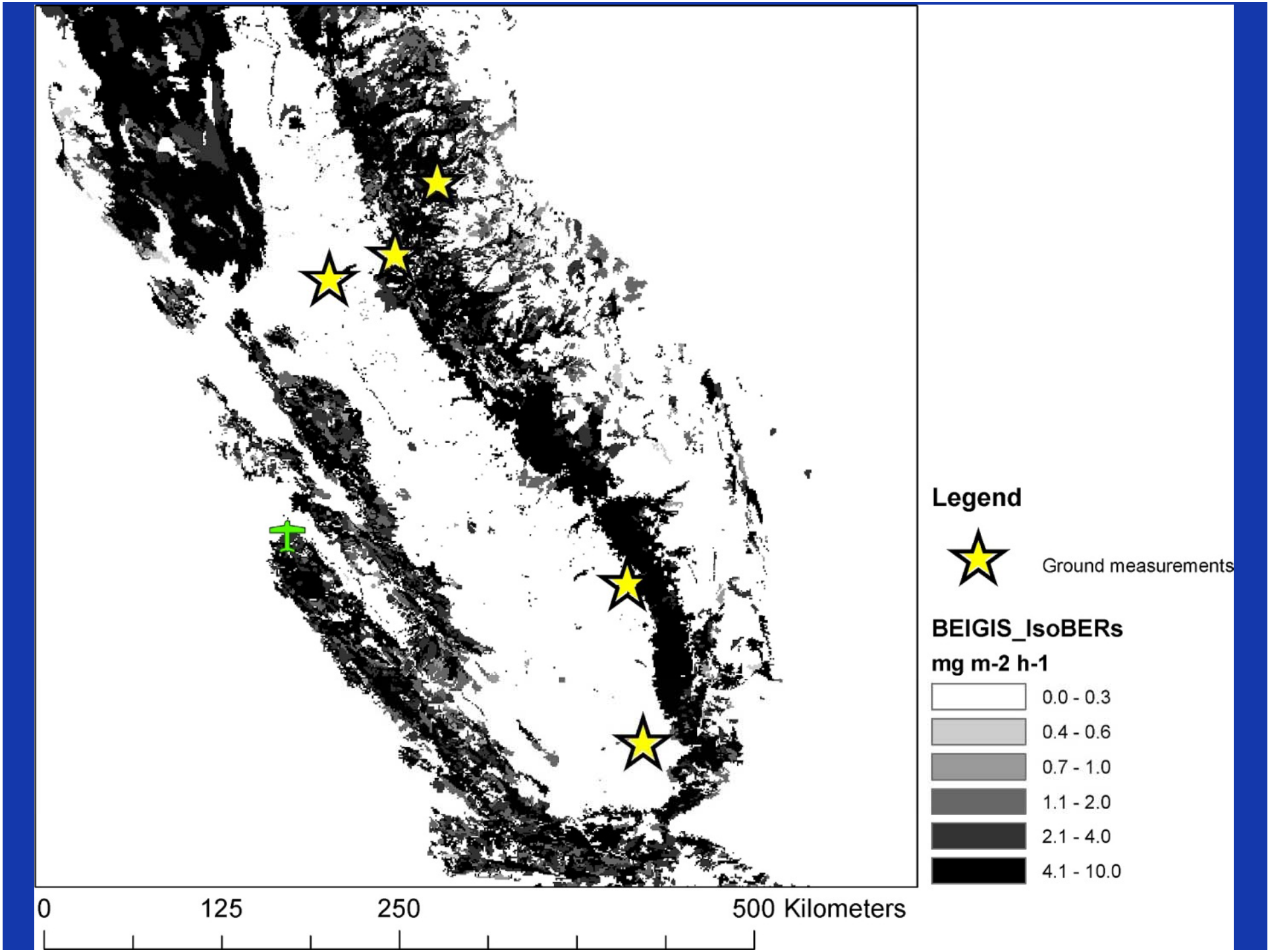

IsoBERs in BEIGIS
mean 2.1 (s.d. 4.0)
mg m-2 h-1
Legend
Ground measurements
BEIGIS_IsoBERs
mg m-2 h-1
0.0 - 0.3
0.4 - 0.6
0.7 - 1.0
1.1 - 2.0
2.1 - 4.0
4.1 - 10.0
0
125
250
500 Kilometers

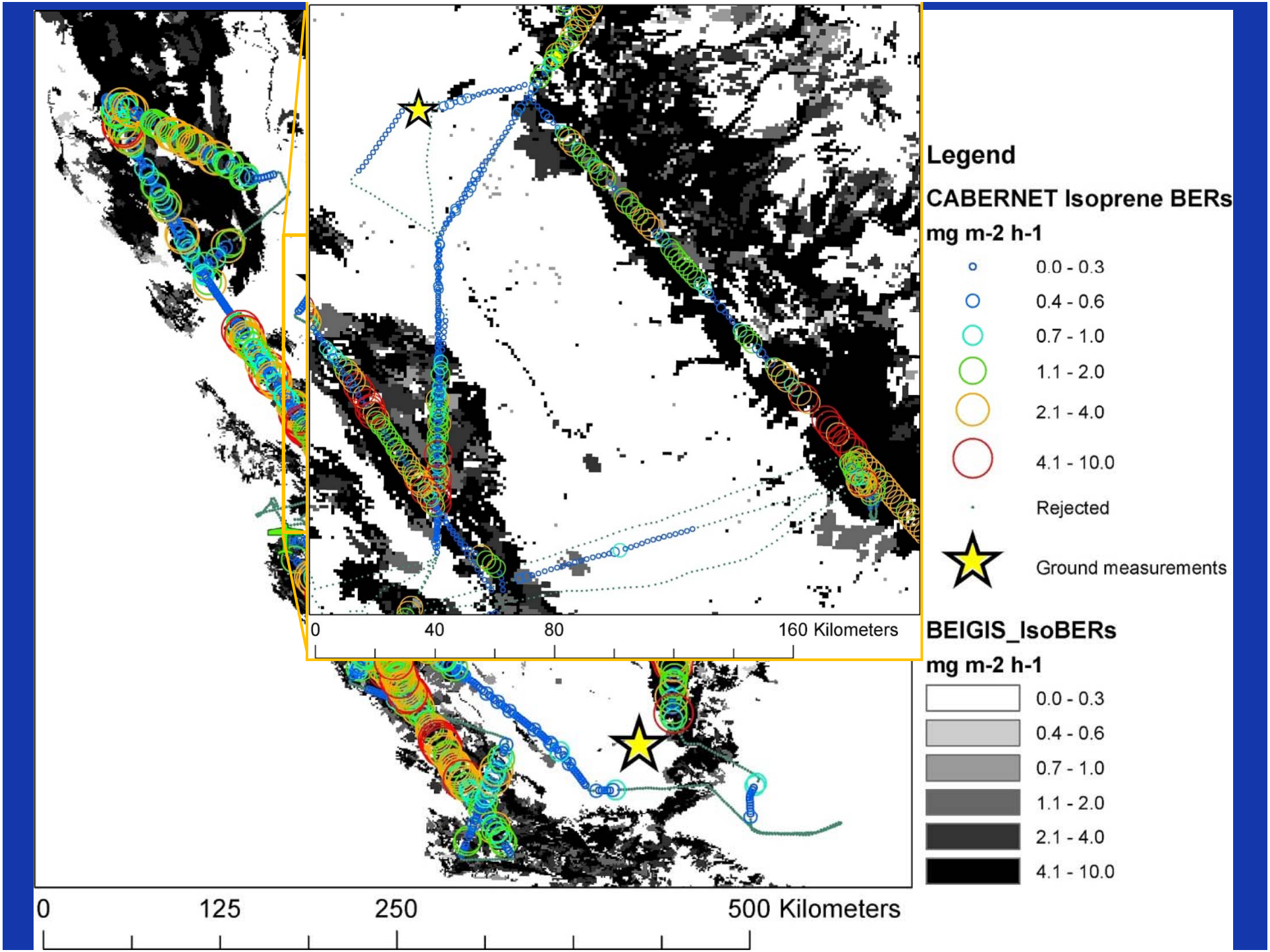

IsoBERs Megan 2.1
Legend
measurements
MEGAN 2.1 landcov2.2
mg m-2 h-1
0.0 - 0.3
0.4 - 0.6
0.7 - 1.0
1.1 - 2.0
2.1 - 4.0
4.1 - 10.0
0
125
250
500 Kilometers

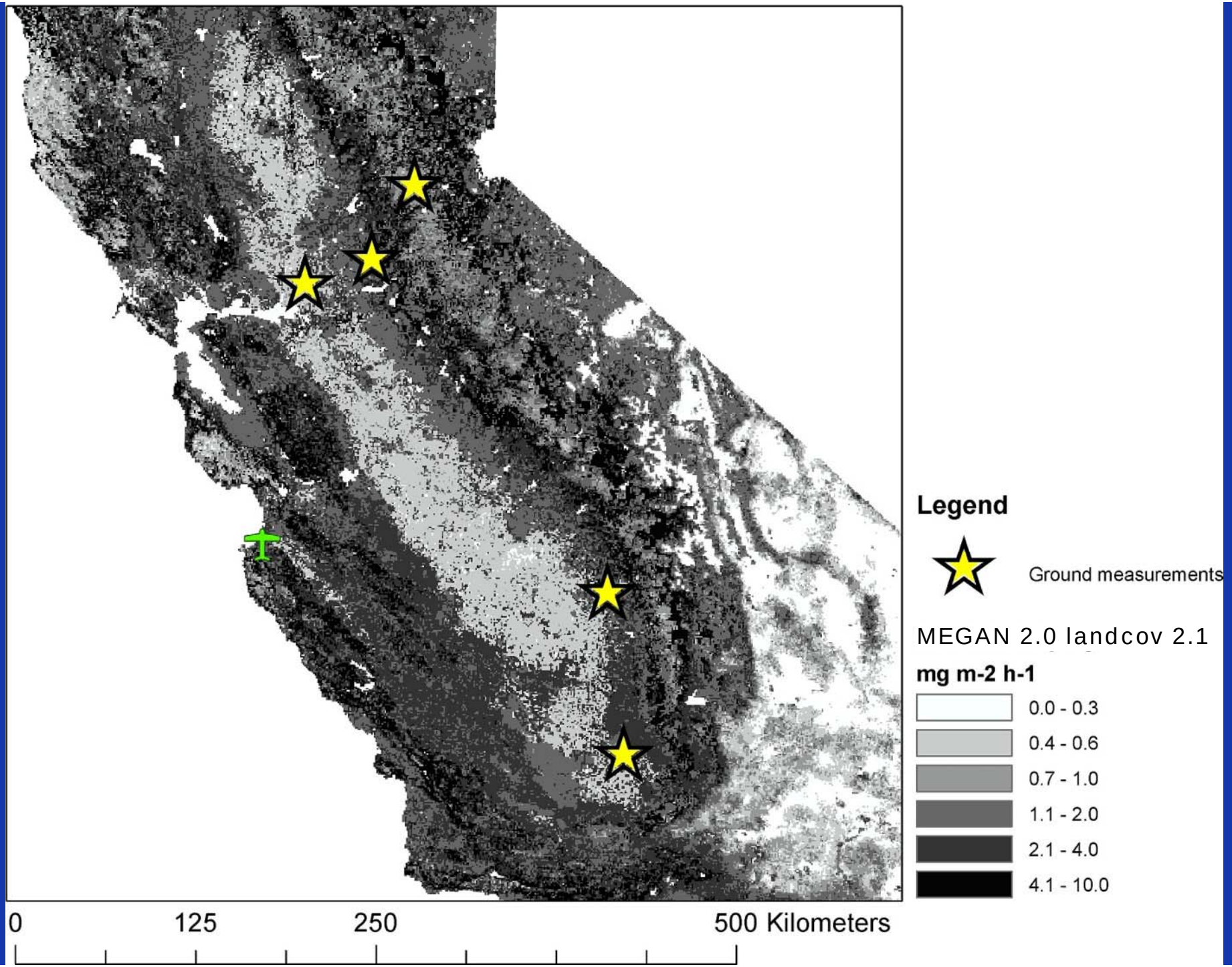

IsoBERs Megan 2.0
mean 2.1 (s.d. 1.9)
mg m-2 h-1
Legend
Ground measurements
MEGAN CAproj
mg m-2 h-1
0.0 - 0.3
0.4 - 0.6
0.7 - 1.0
1.1 - 2.0
2.1 - 4.0
4.1 - 10.0
0
125
250
500 Kilometers

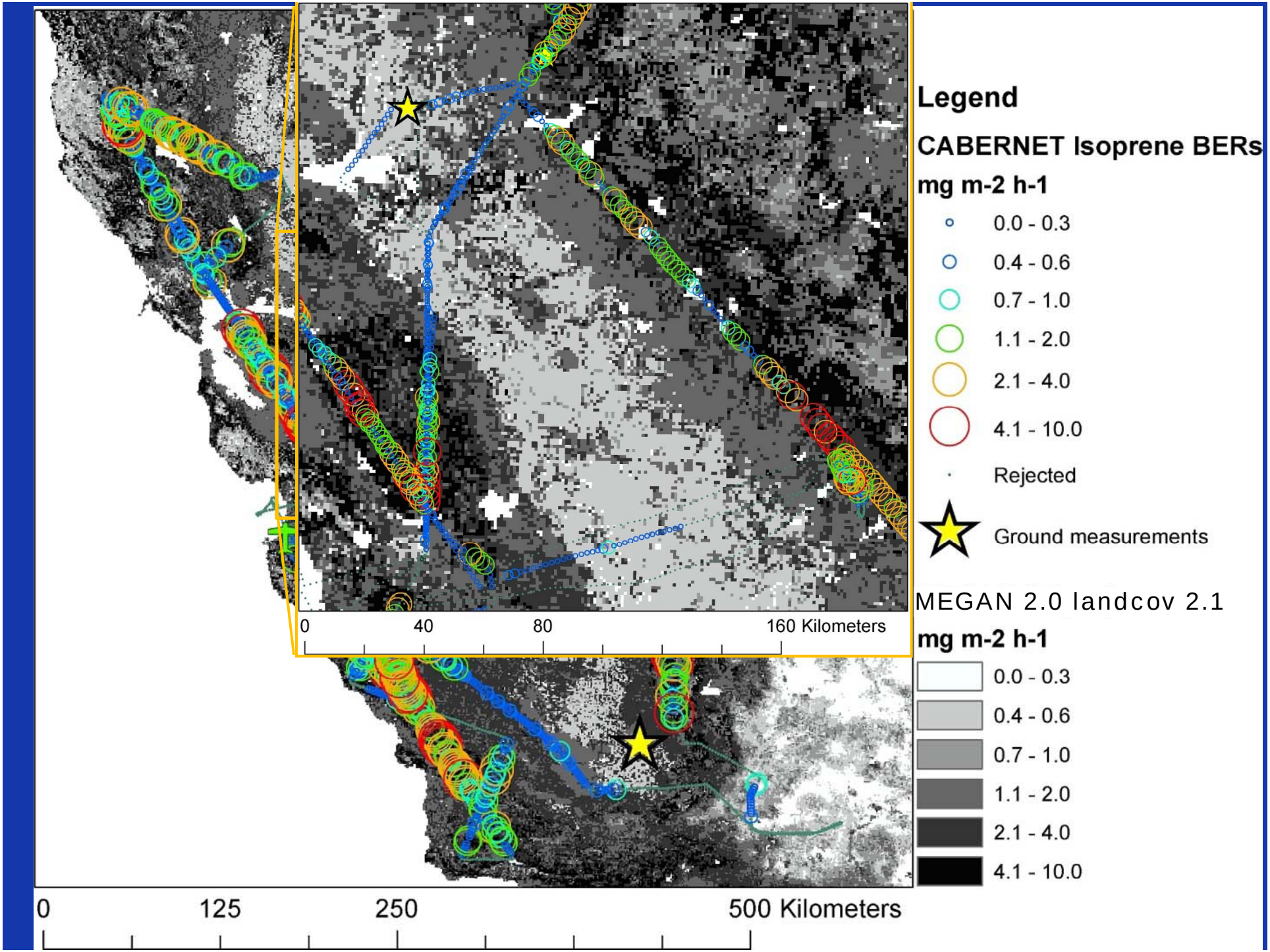

Legend
Oak woodlands (GAP)
%
0 - 10
11 - 30
31 - 50
51 - 70
71 - 100
Ground measurements
0
125
250
500 Kilometers

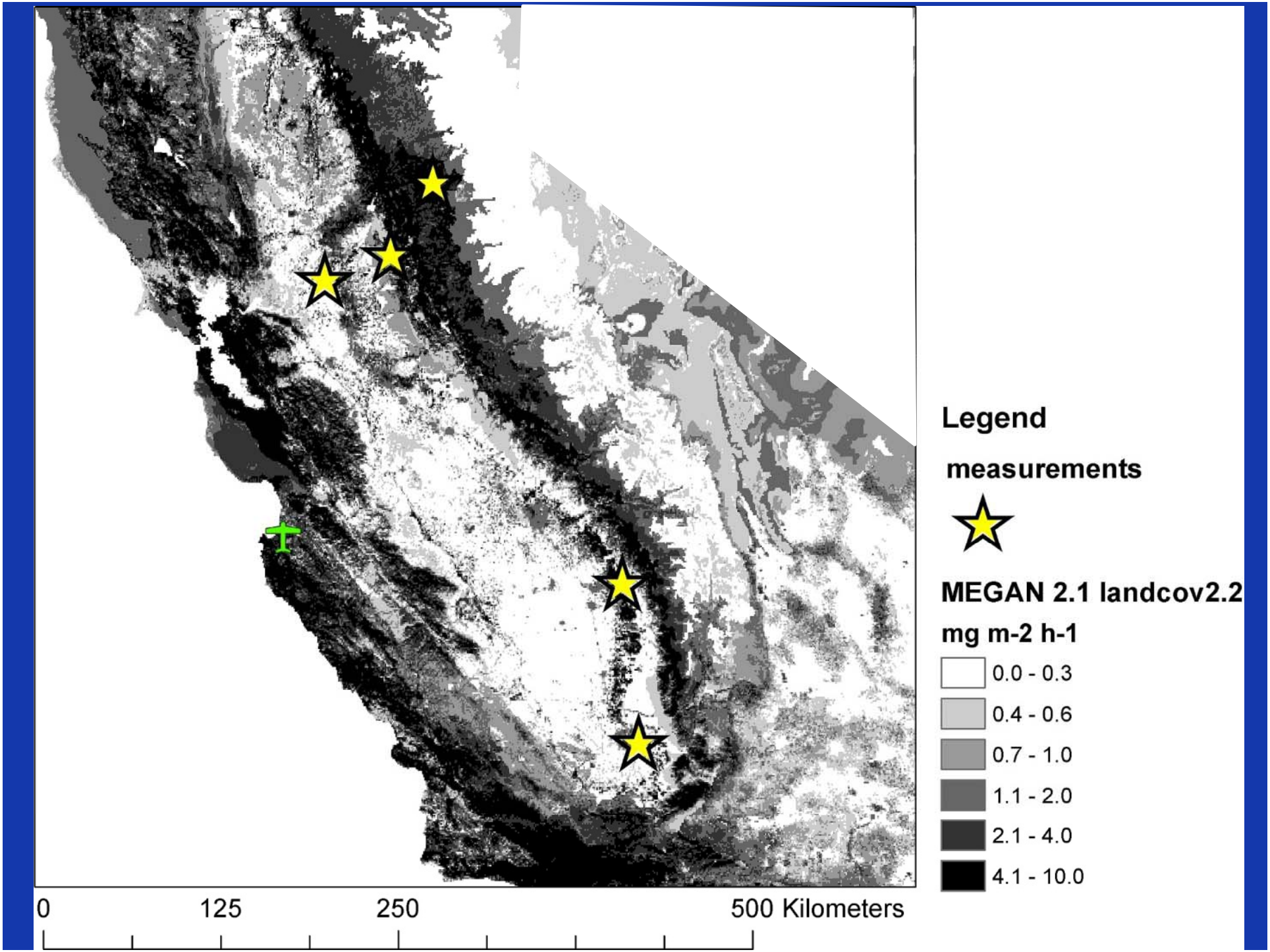

Legend
CABERNET Isoprene BERs
mg m-2 h-1
0.0 - 0.3
0.4 - 0.6
0.7 - 1.0
1.1 - 2.0
2.1 - 4.0
4.1 - 10.0
Rejected
Ground measurements
Oak woodlands (GAP)
%
0 - 10
11 - 30
31 - 50
51 - 70
71 - 100
0
125
250
500 Kilometers

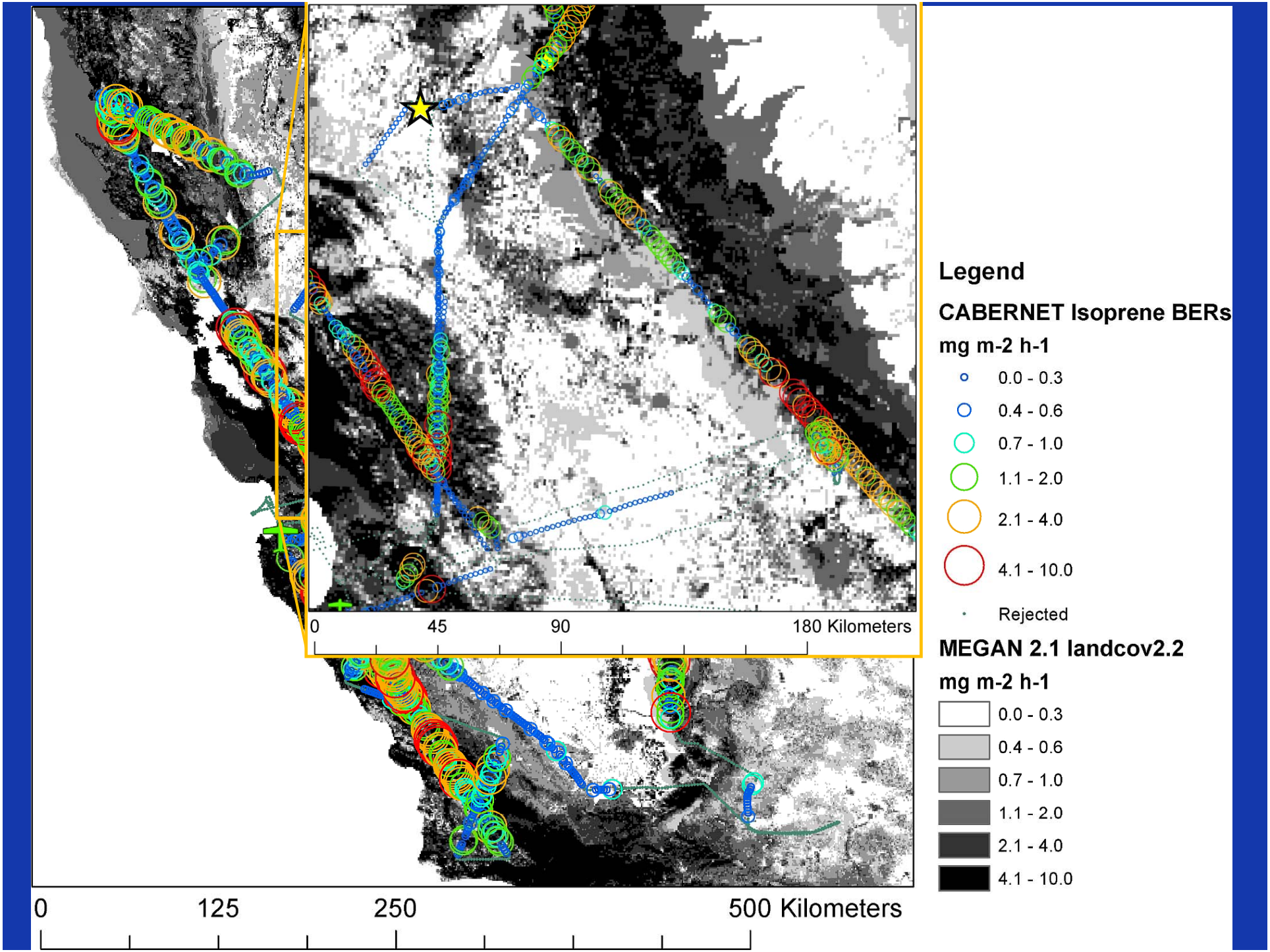

Legend
Ground measurements
BEIGIS_IsoBERs
mg m-2 h-1
0.0 - 0.3
0.4 - 0.6
0.7 - 1.0
1.1 - 2.0
2.1 - 4.0
4.1 - 10.0
0
125
250
500 Kilometers


Legend
CABERNET Isoprene BERs
mg m-2 h-1
0.0 - 0.3
0.4 - 0.6
0.7 - 1.0
1.1 - 2.0
2.1 - 4.0
4.1 - 10.0
Rejected
Ground measurements
BEIGIS_IsoBERs
mg m-2 h-1
0.0 - 0.3
0.4 - 0.6
0.7 - 1.0
1.1 - 2.0
2.1 - 4.0
4.1 - 10.0
0
40
80
160 Kilometers
0
125
250
500 Kilometers

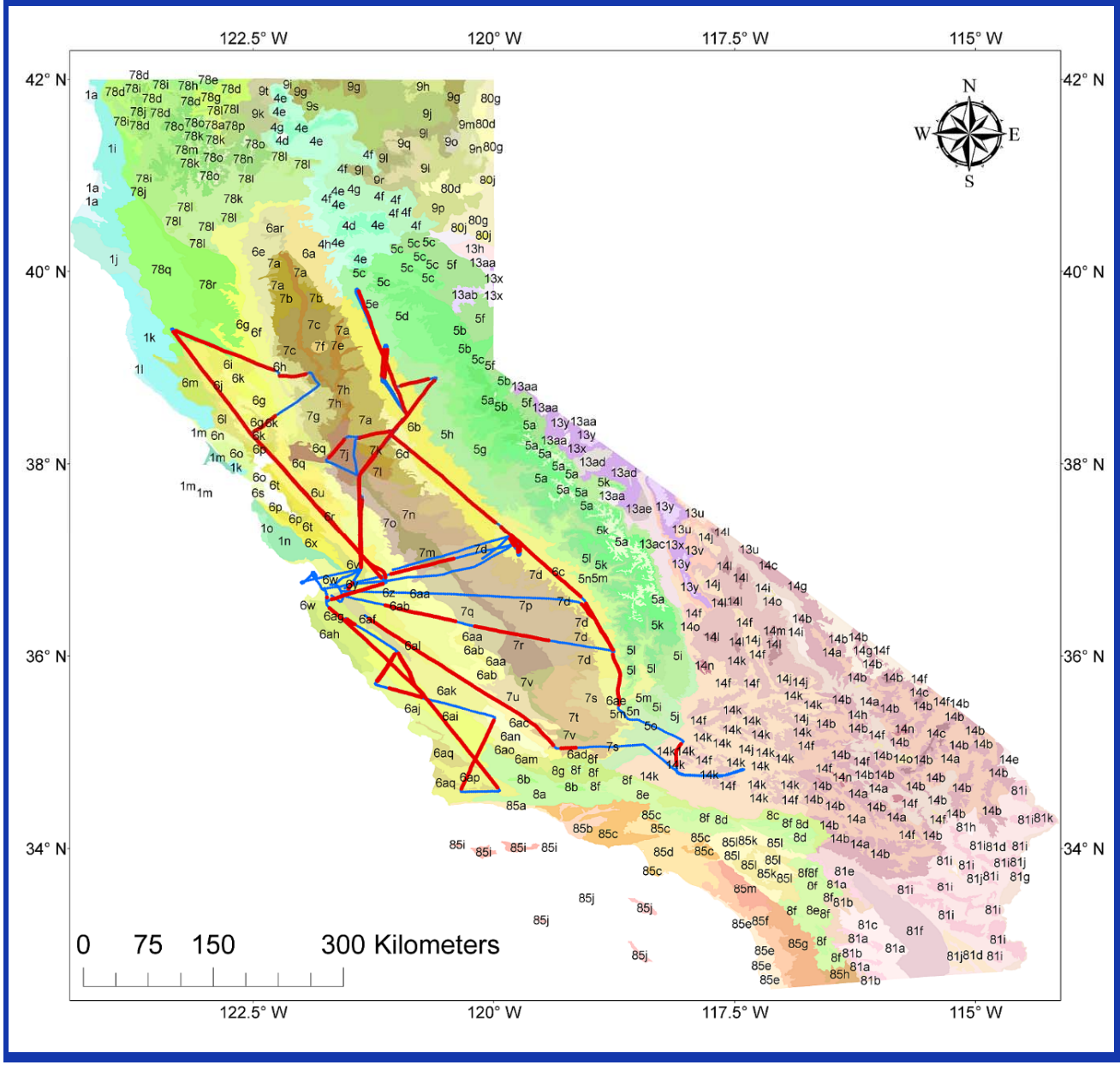

Legend
Ground measurements
MEGAN 2.0 landcov 2.1
mg m-2 h-1
0.0 - 0.3
0.4 - 0.6
0.7 - 1.0
1.1 - 2.0
2.1 - 4.0
4.1 - 10.0
0
125
250
500 Kilometers


Legend
CABERNET Isoprene BERs
mg m-2 h-1
0.0 - 0.3
0.4 - 0.6
0.7 - 1.0
1.1 - 2.0
2.1 - 4.0
4.1 - 10.0
Rejected
Ground measurements
MEGAN 2.0 landcov 2.1
mg m-2 h-1
0.0 - 0.3
0.4 - 0.6
0.7 - 1.0
1.1 - 2.0
2.1 - 4.0
4.1 - 10.0
0
40
80
160 Kilometers
0
125
250
500 Kilometers


Legend
measurements
MEGAN 2.1 landcov2.2
mg m-2 h-1
0.0 - 0.3
0.4 - 0.6
0.7 - 1.0
1.1 - 2.0
2.1 - 4.0
4.1 - 10.0
0
125
250
500 Kilometers

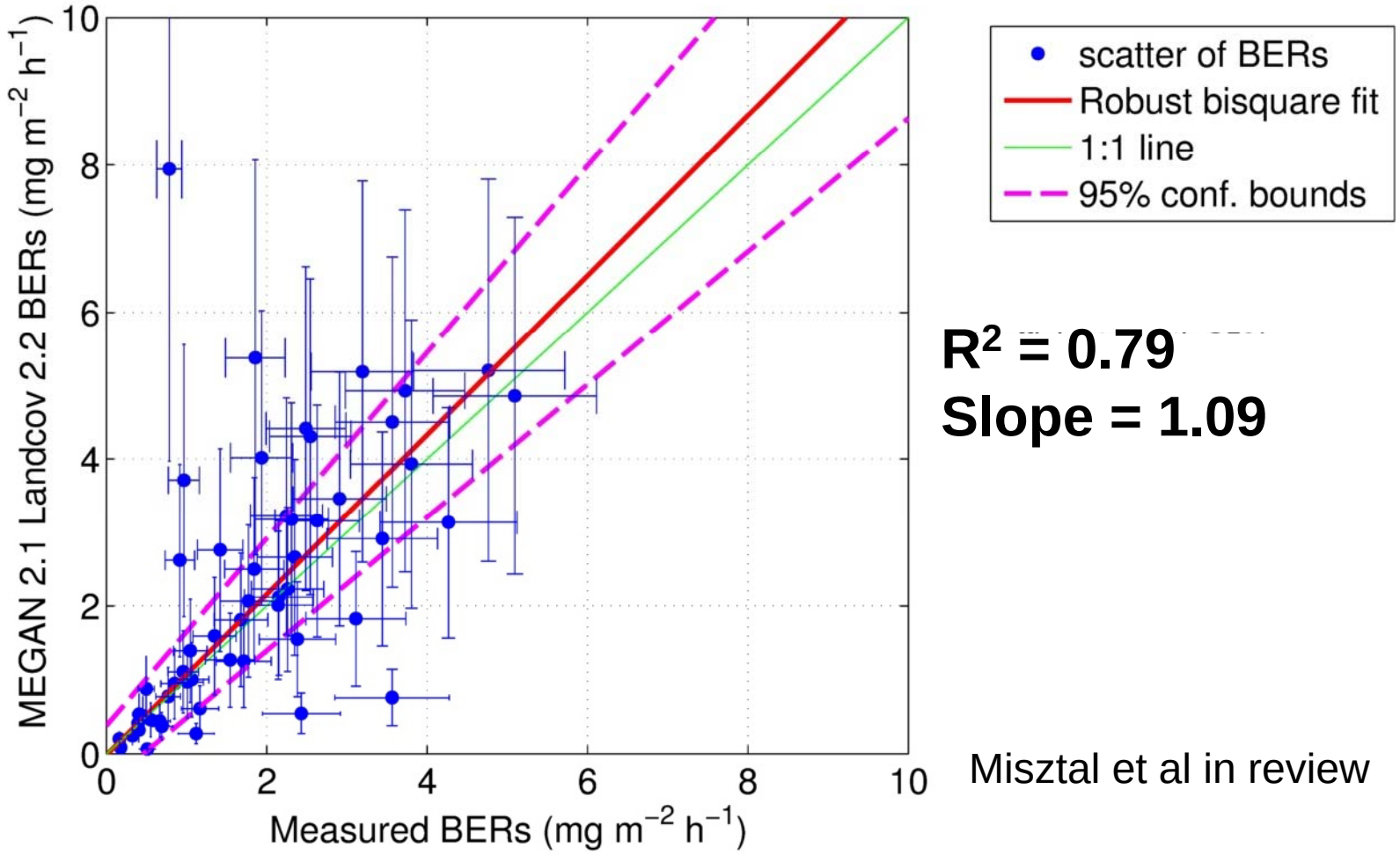

Legend
CABERNET Isoprene BERs
mg m-2 h-1
0.0 - 0.3
0.4 - 0.6
0.7 - 1.0
1.1 - 2.0
2.1 - 4.0
4.1 - 10.0
Rejected
MEGAN 2.1 landcov2.2
mg m-2 h-1
0.0 - 0.3
0.4 - 0.6
0.7 - 1.0
1.1 - 2.0
2.1 - 4.0
4.1 - 10.0
0
45
90
180 Kilometers
0
125
250
500 Kilometers

US EPA Ecoregions - areas of general similarity in ecosystems and in the type, quality, and quantity of environmental resources



5d Northern Sierra Mid-Montane Forests
5e Northern Sierra Lower Montane Forests
5f Northeastern Sierra Mixed Conifer-Pine Forests
5g Central Sierra Mid-Montane Forests
5h Central Sierra Lower Montane Forests
5i Eastern Sierra Great Basin Slopes
5j Eastern Sierra Mojavean Slopes
5k Southern Sierra Subalpine Forests
5l Southern Sierra Upper Montane Forests
5m Southern Sierra Mid-Montane Forests
5n Southern Sierra Lower Montane Forest and Woodland
5o Tehachapi Mountains
6a Tuscan Flows
6aa Eastern Hills
6ab Pleasant Valley/Kettleman Plain
6ac Temblor Range/Elk Hills
6ad Grapevine Transition
6ae Tehachapi Foothills
6af Salinas Valley
6ag Northern Santa Lucia Range
6ah Santa Lucia Coastal Forest and Woodland
6ai Interior Santa Lucia Range
6aj Southern Santa Lucia Range
6ak Paso Robles Hills and Valleys
6al Salinas-Cholame Hills
6am Cuyama Valley
6an Carrizo Plain
6ao Caliente Range
6ap Solomon-Purisima-Santa Ynez Hills
6aq Santa Maria/Santa Ynez Valleys
6ar Upper Sacramento River Alluvium
6b Northern Sierran Foothills
6c Southern Sierran Foothills
6d Camanche Terraces
6e Tehama Terraces
6f Foothill Ridges and Valleys
6g North Coast Range Eastern Slopes
6h Western Valley Foothills/Dunnigan Hills
6i Clear Lake Hills and Valleys
6j Mayacmas Mountains
6k Napa-Sonoma-Lake Volcanic Highlands
6l Napa-Sonoma-Russian River Valleys
6m Sonoma-Mendocino Mixed Forest
6n Bodega Coastal Hills
6o Marin Hills
6p Bay Flats
6q Suisun Terraces and Low Hills

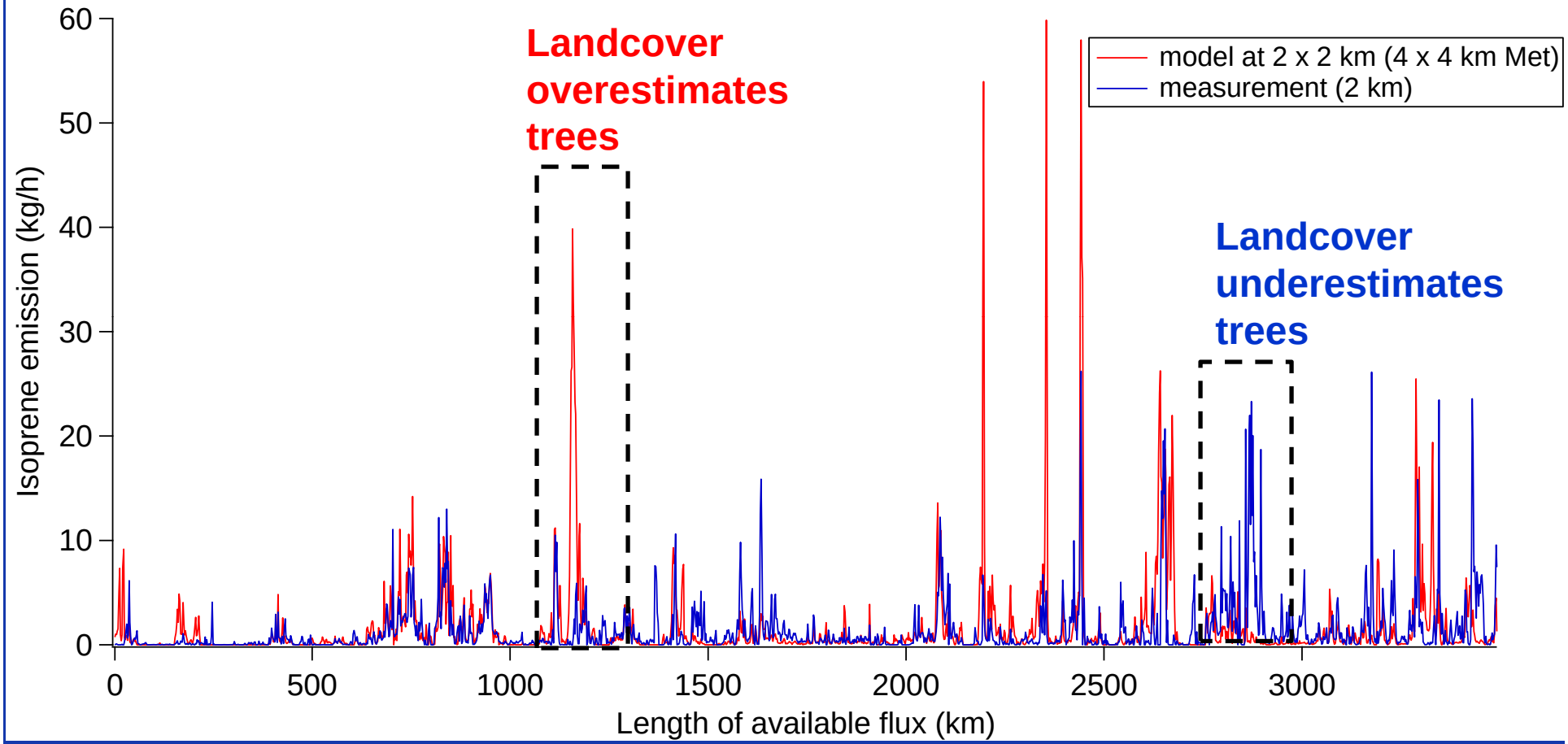
MEGAN 2.1 Land 2.2 vs CABERNET BERs



Misztal et al in review

On average Megan 2.1 Land 2.2 BER's agree well with observations (within 9%).

Current CARB Model (BEIGIS landcover) emissions vs CABERNET Fluxes



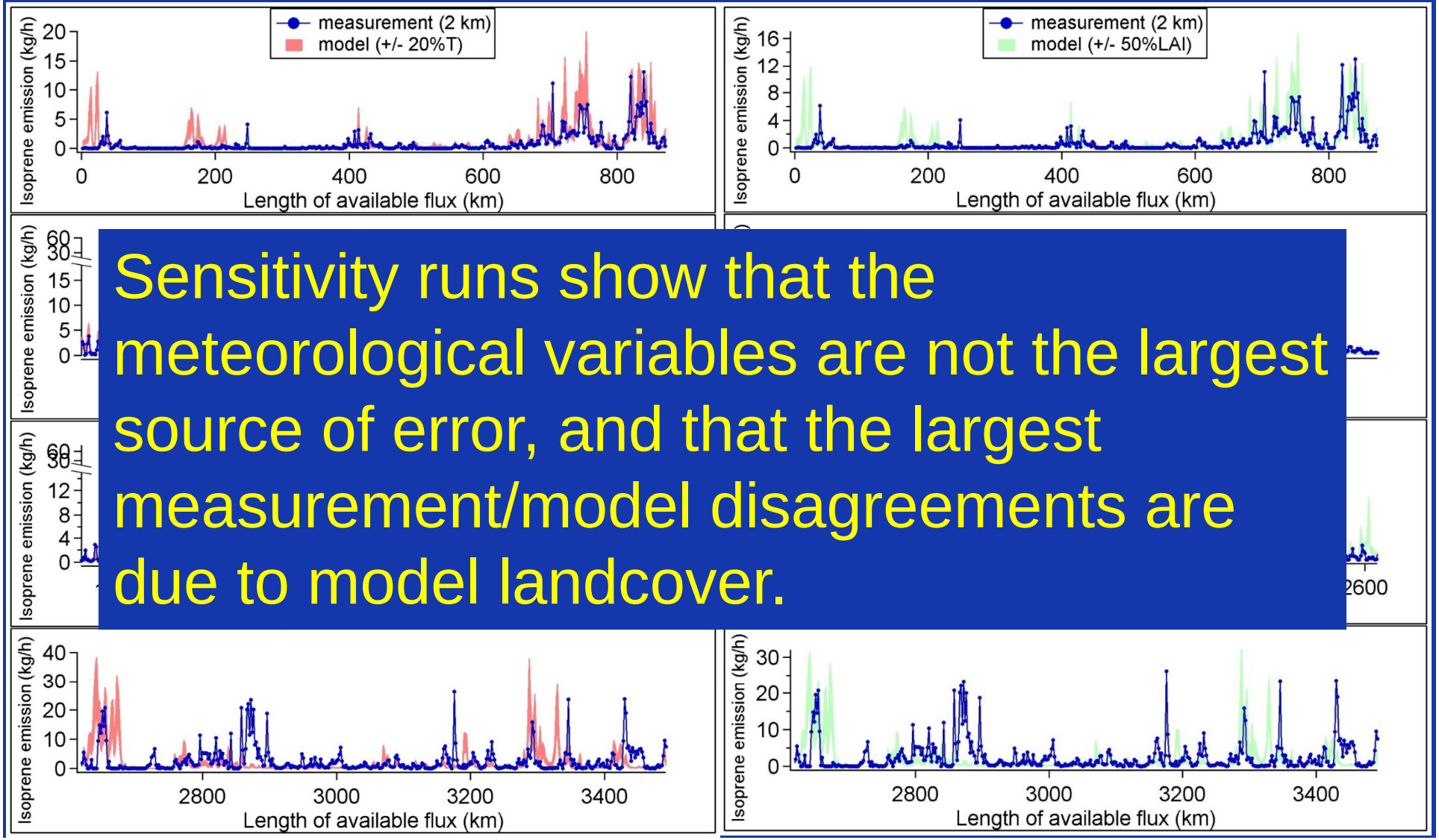
Good agreement in most places, but Landcover 2.2 is more accurate. Discrepancies indicate where landcover needs improvement.

Misztal et al in review

Sensitivities to temperature and LAI show relatively small effects

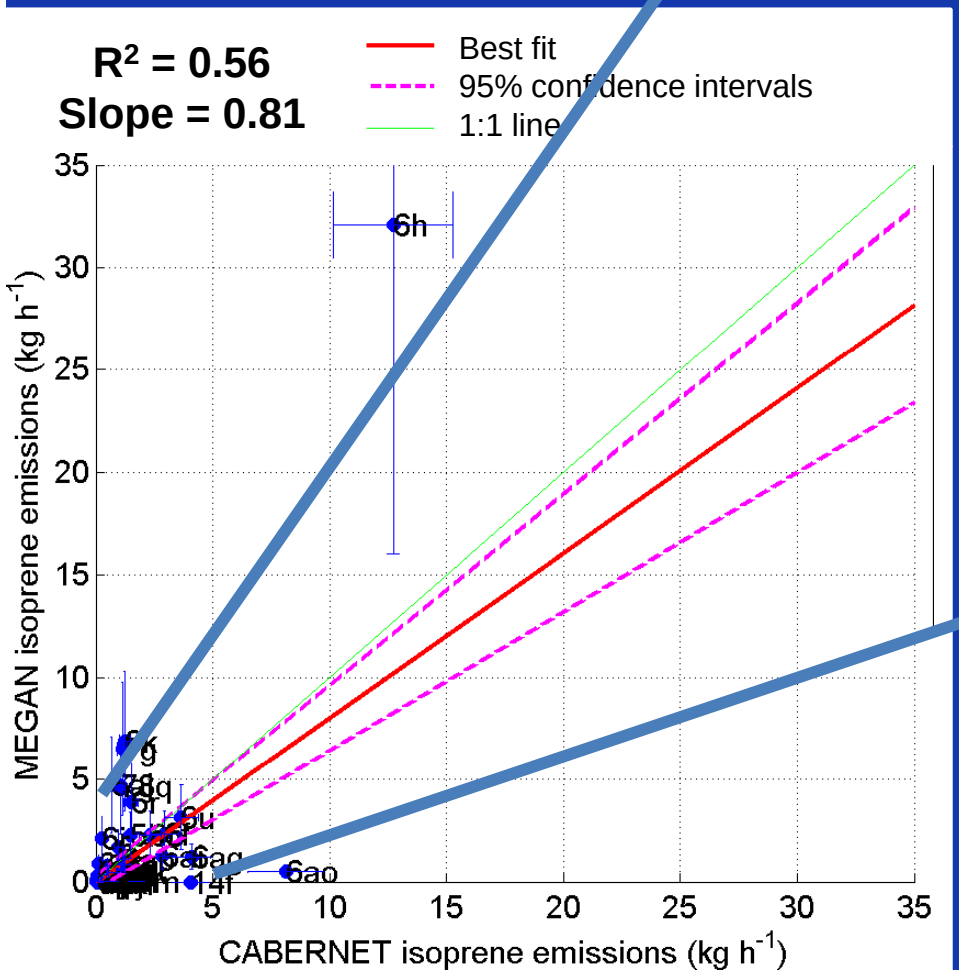
+/- 20% temperature

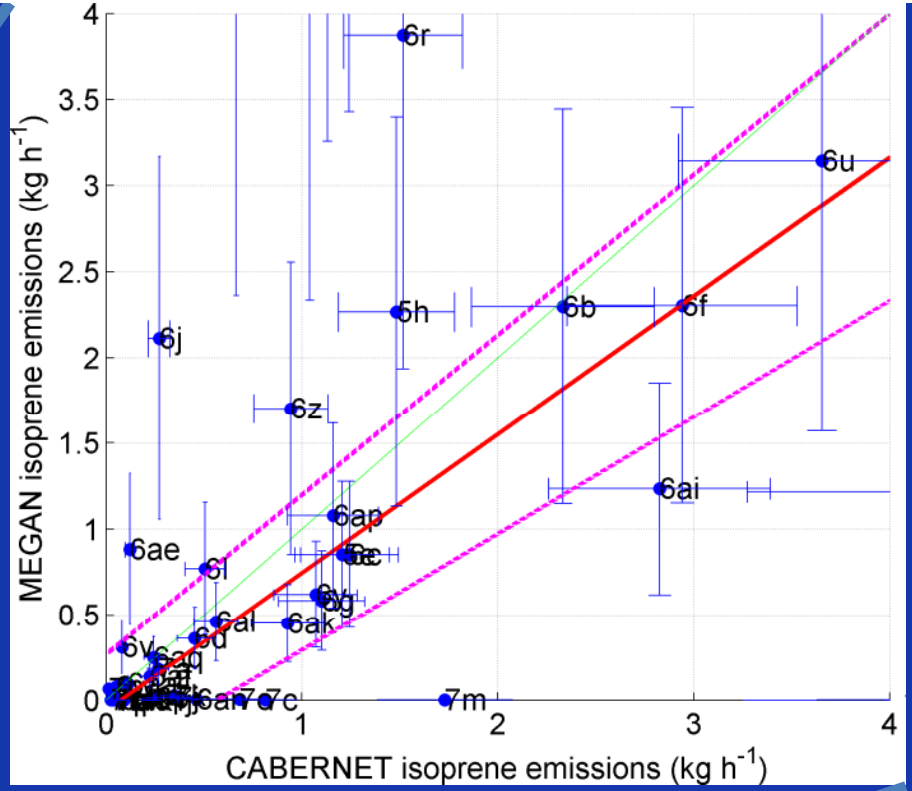
+/- 50% LAI



Sensitivity runs show that the meteorological variables are not the largest source of error, and that the largest measurement/model disagreements are due to model landcover.

Measured emission vs CARB Model (BEIGIS Landcover) Averaged by Ecoregion





CARB model showed good agreement on average, underestimating ecoregion averaged measurements by 19% over the whole dataset.

50% of ecoregions agreement was within 50%

21% of ecoregions model overestimate > 50%

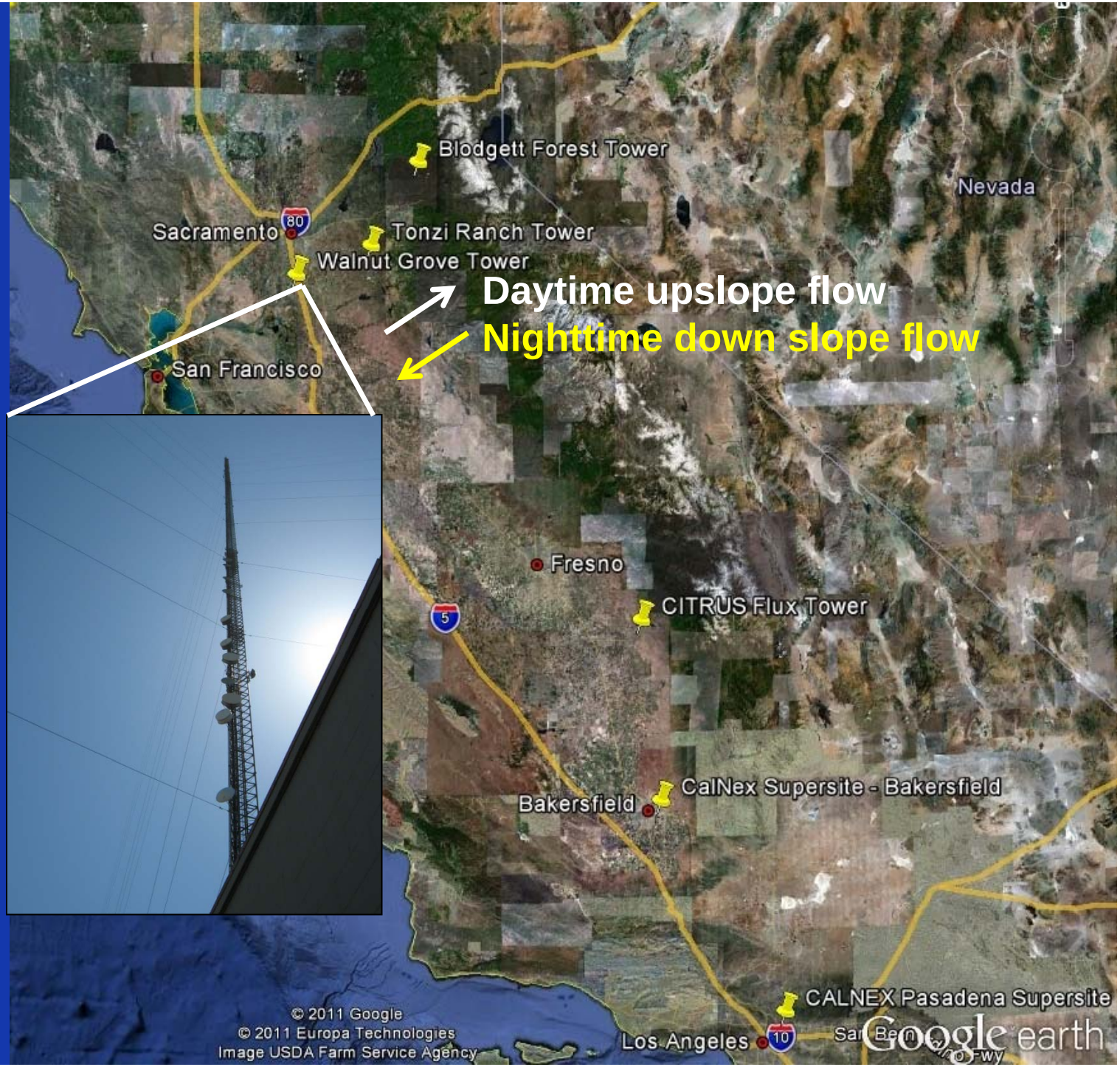
29% of ecoregions model underestimate < 50%

Agreement was generally better for ecoregions with more extensive measurements

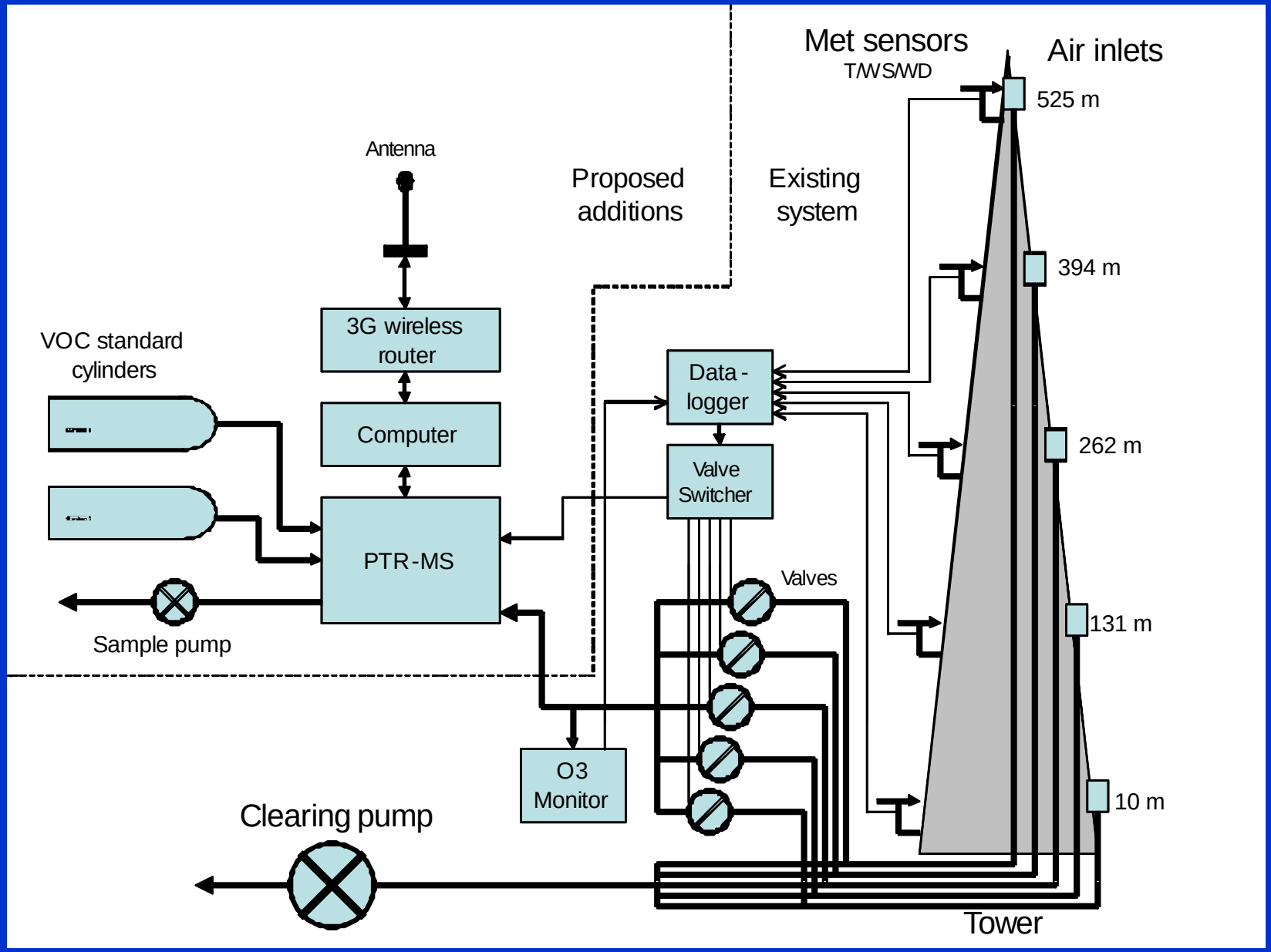
TALL TOWER Walnut Grove

PTRMS vertical profiles of 20 masses every 10 minutes

5 Sample inlets from 10-525 m

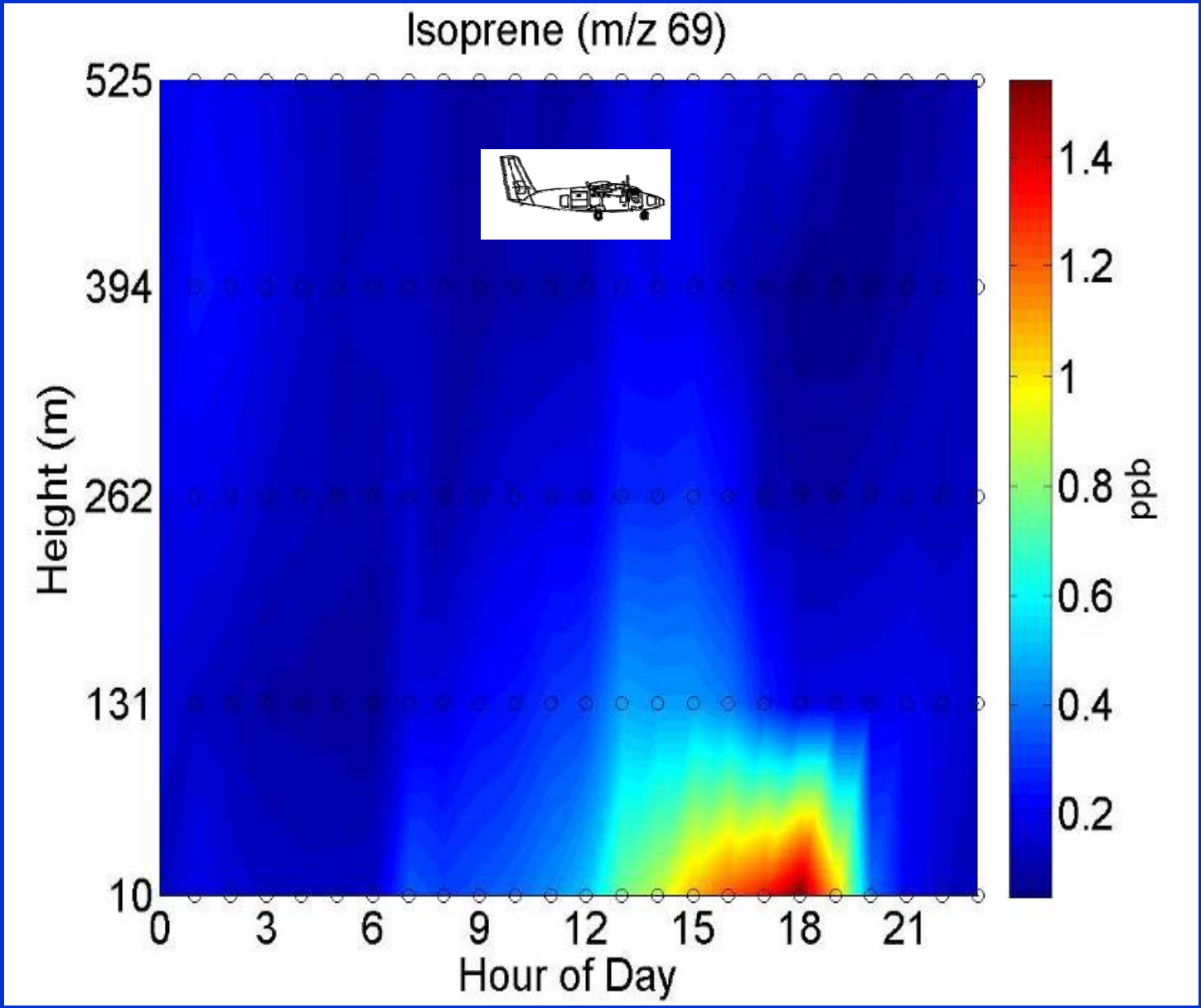


Walnut Grove Tower: Measurement Setup

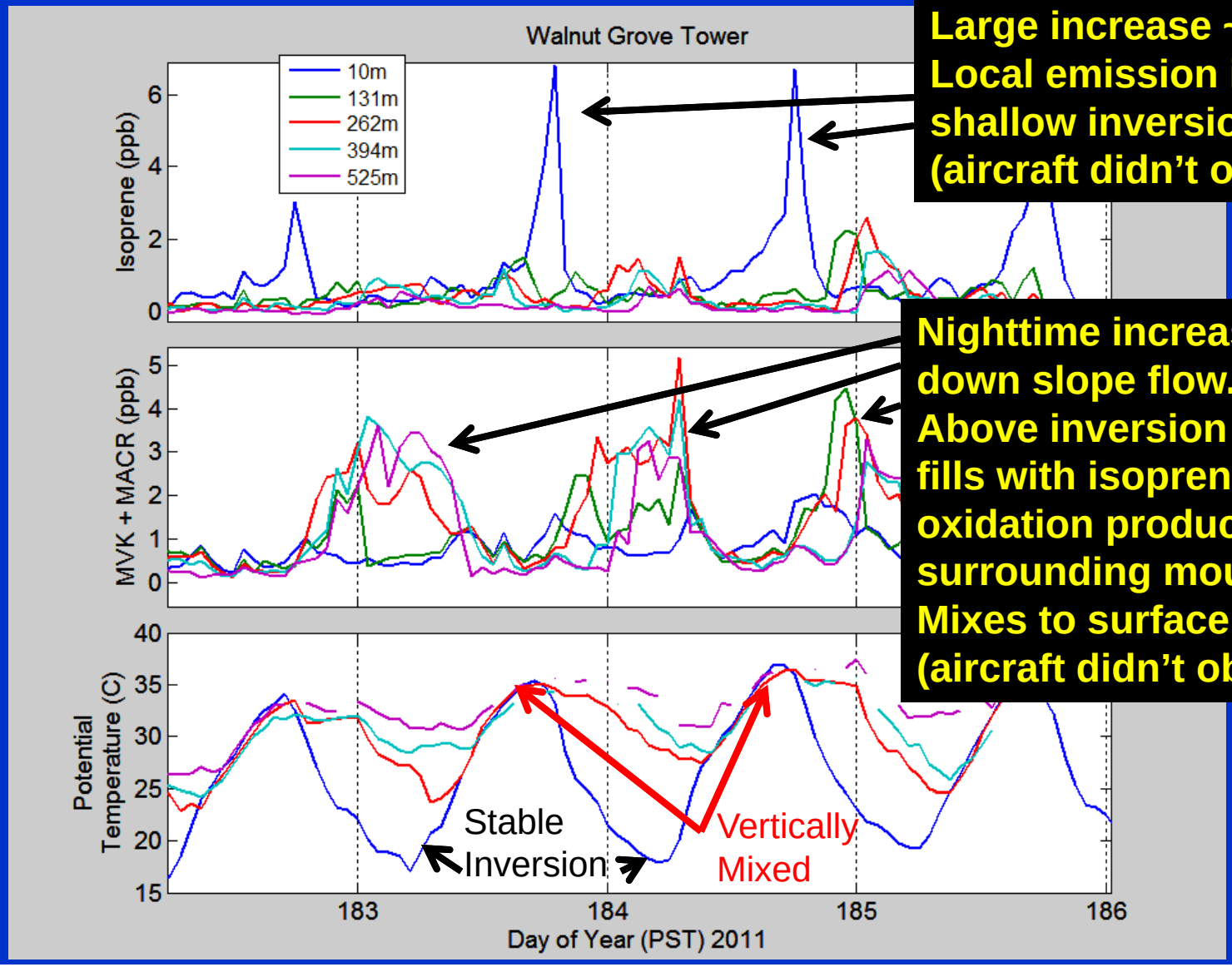


Measurements June-Aug 2011; June 2012 –September 2013

Ground-Aircraft Comparison



Potential Temperature Gradient
→ Indicator of Vertical Mixing
Separates Local Versus Transported BVOC



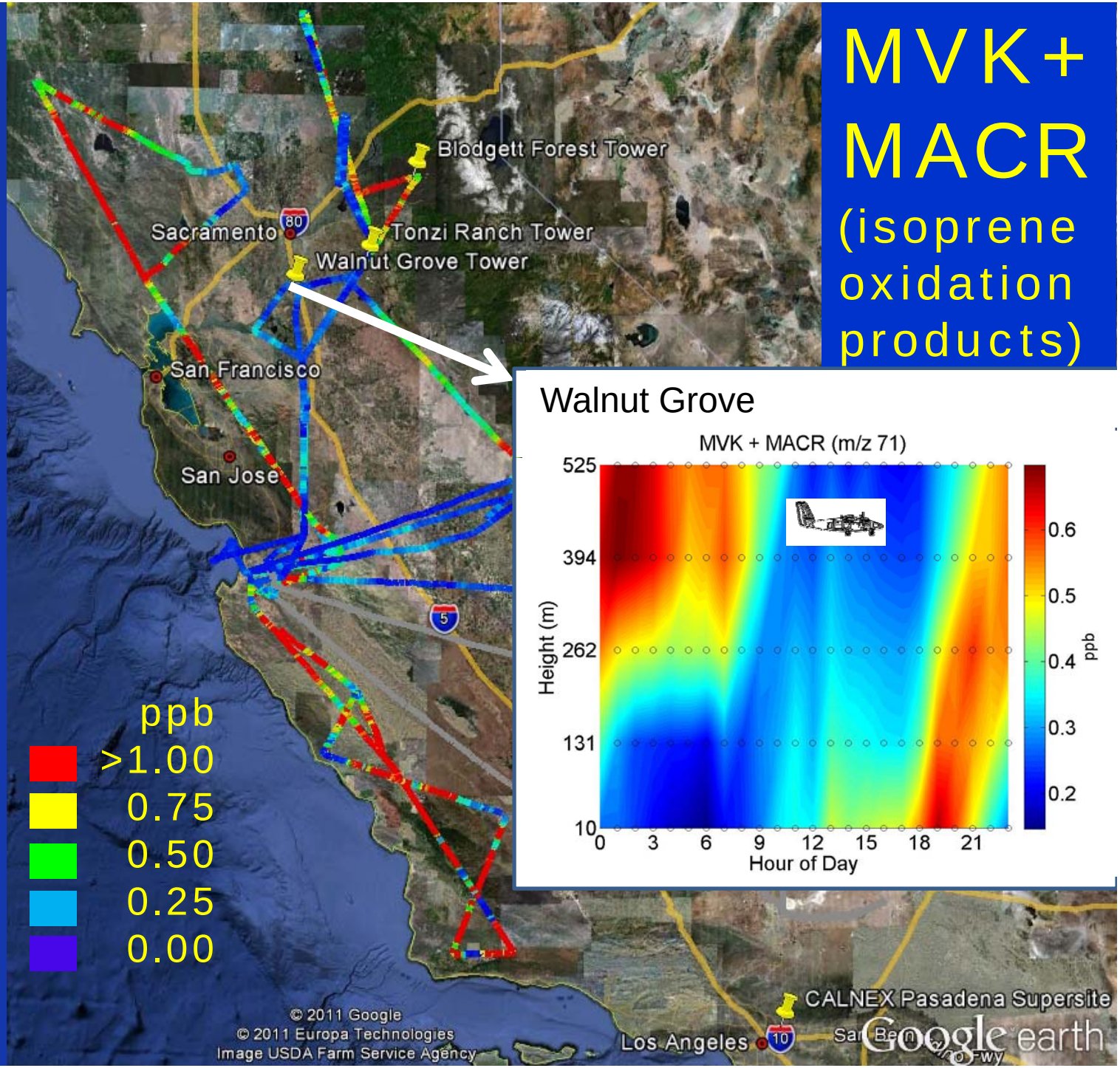
Large increase ~6 pm. Local emission into shallow inversion. (aircraft didn't observe)

Nighttime increase with down slope flow. Above inversion valley fills with isoprene and oxidation products from surrounding mountains. Mixes to surface in a.m. (aircraft didn't observe)

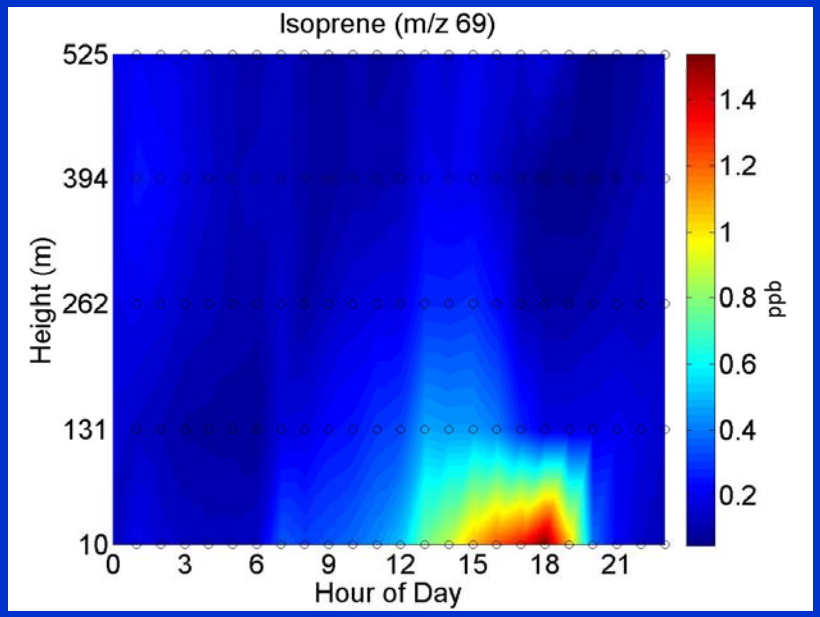
MVK+ MACR (isoprene oxidation products)

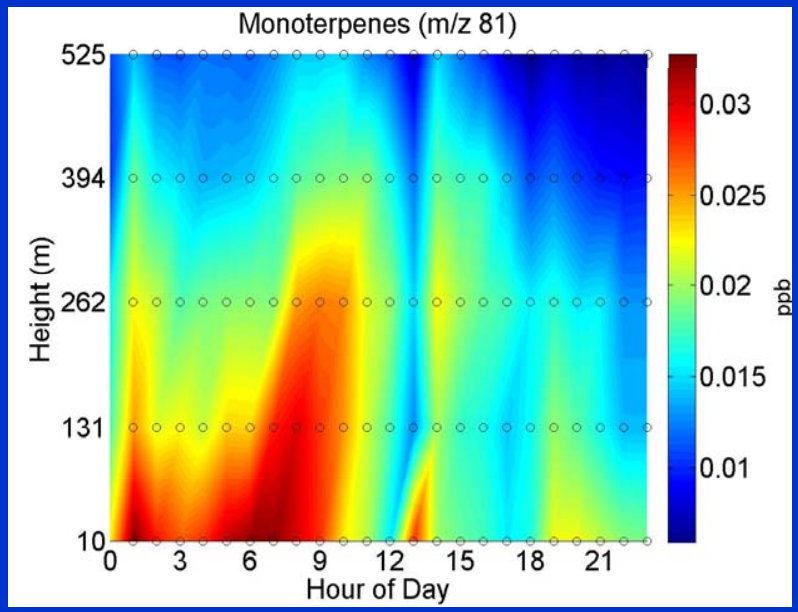
Aircraft observed high MVK+MACR over hills & mountains, low over valley during daytime.

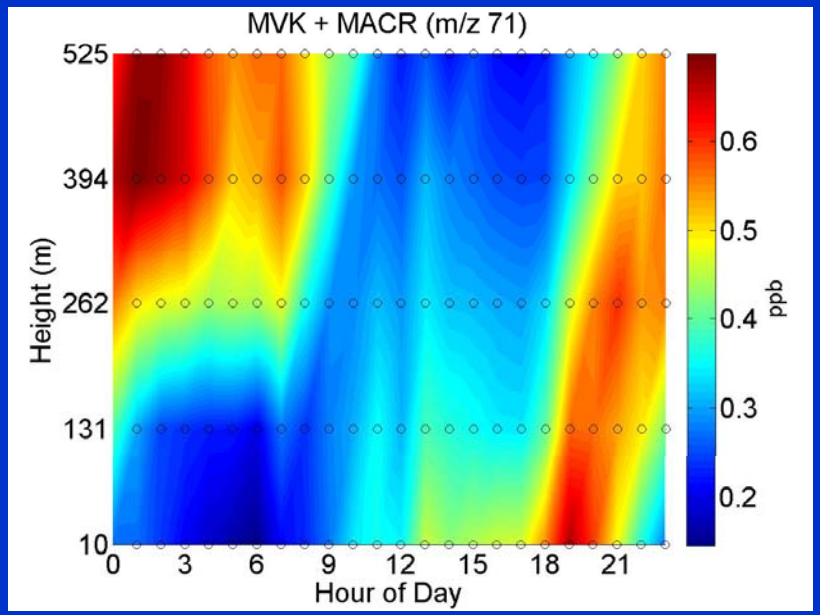
Above inversion valley fills with isoprene and oxidation products at night from surrounding mountains. Mixes to surface in a.m. (aircraft didn't observe)

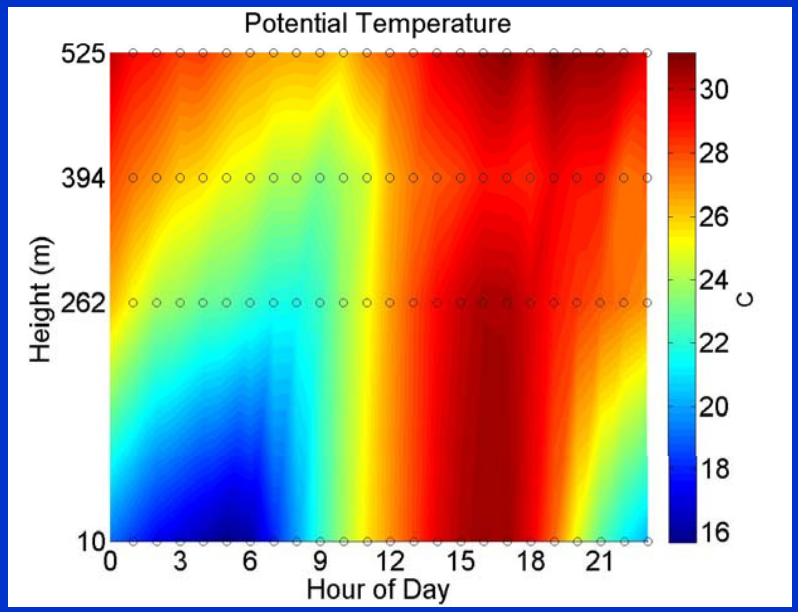


Average Vertical Profiles at Walnut Grove June-Aug 2011









Conclusions

•Oak woodlands confirmed to be dominant isoprene emission sources in CA.

•Spatial resolution of temperature used in model is very important, particularly in foothills where Oak woodlands dominate the landscape.

•Largest uncertainty in modeling isoprene fluxes for CA is the landcover input.

•MEGAN landcover 2.2 BER's were most accurate, agreeing with measured BER's within 9% averaged by ecoregion.

•CARB's model using BEIGIS landcover showed reasonable agreement with ecoregion averaged flux measurements, underestimating by 19% over the whole dataset, and agreeing within 50% for half of the ecoregions.

•We recommend CARB use MEGAN landcover 2.2 for future BVOC modeling.

•Continuous measurements at Walnut Grove complement aircraft to elucidate temporal and vertical distribution of isoprene + products in CA's Central Valley.

Promising Future Directions for Landscape Scale Flux Observations from Aircraft?

Spatial distribution of fluxes over different landscapes and seasons
→ need to verify emission inventories in different seasons (e.g. peak ozone season), and improve emission models for a wide variety of landscapes (forest, agriculture, oil/gas fields, urban, etc).

Increase range of observed VOC fluxes and oxidation products
→ improved measurement techniques are now available (high res PTR-ToF-MS, additional CIMS instruments) that enable simultaneous measurements of a very comprehensive array of VOCs.

Bidirectional exchange
→ deposition rates of oxidized VOC are largely unknown and critically important for understanding atmospheric VOC budget. New measurements are needed.

Greenhouse gases
→ Expand the scope of measurements to include GHG's: CH_4, CO_2, and possibly N_2O. Could also include NOx/NOy, CO, or other species for which fast measurements are available and emission inventories need verification.

Acknowledgements

California Air Resources Board (CARB),
CIRPAS team for help in instrument integration,
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