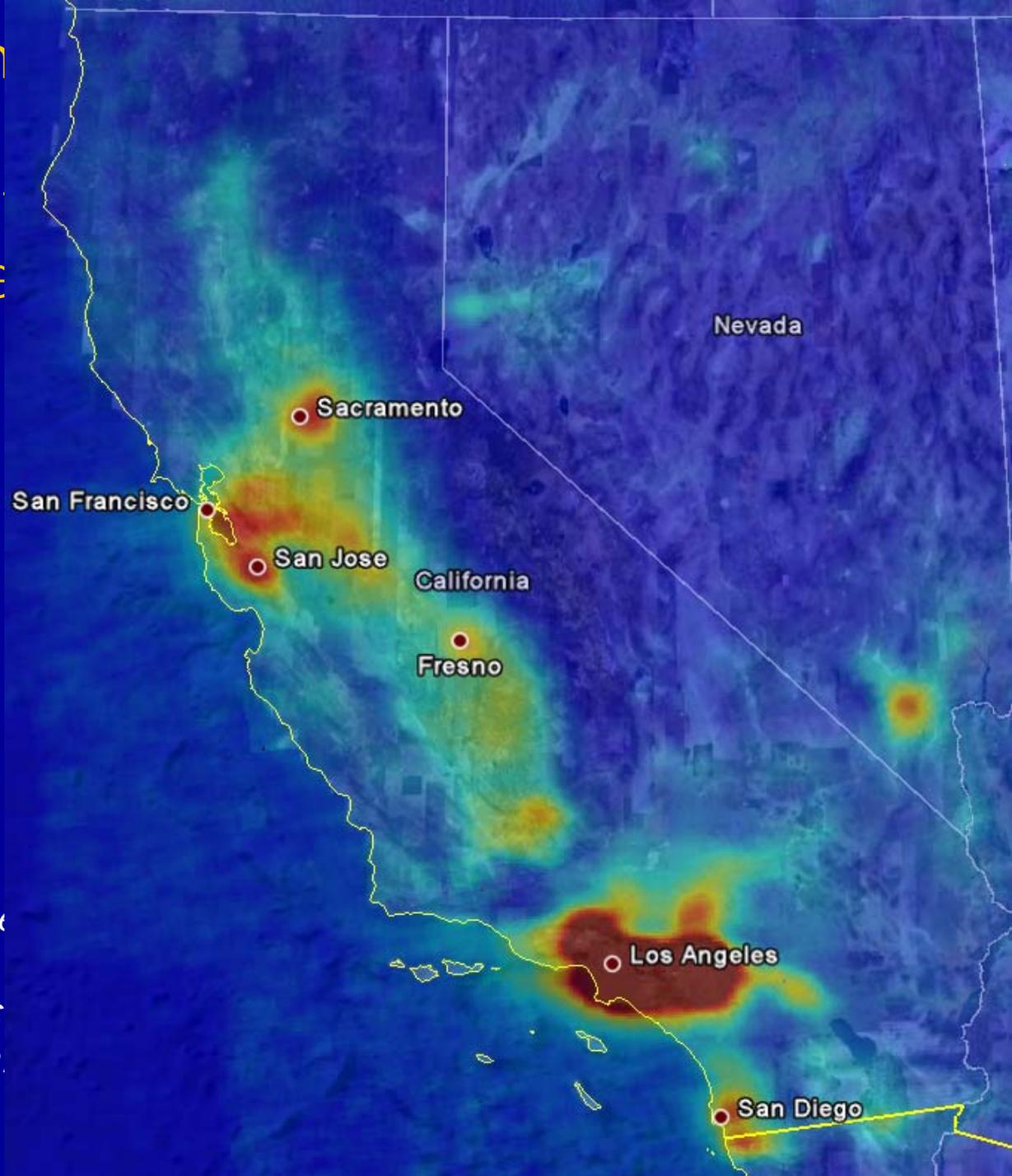


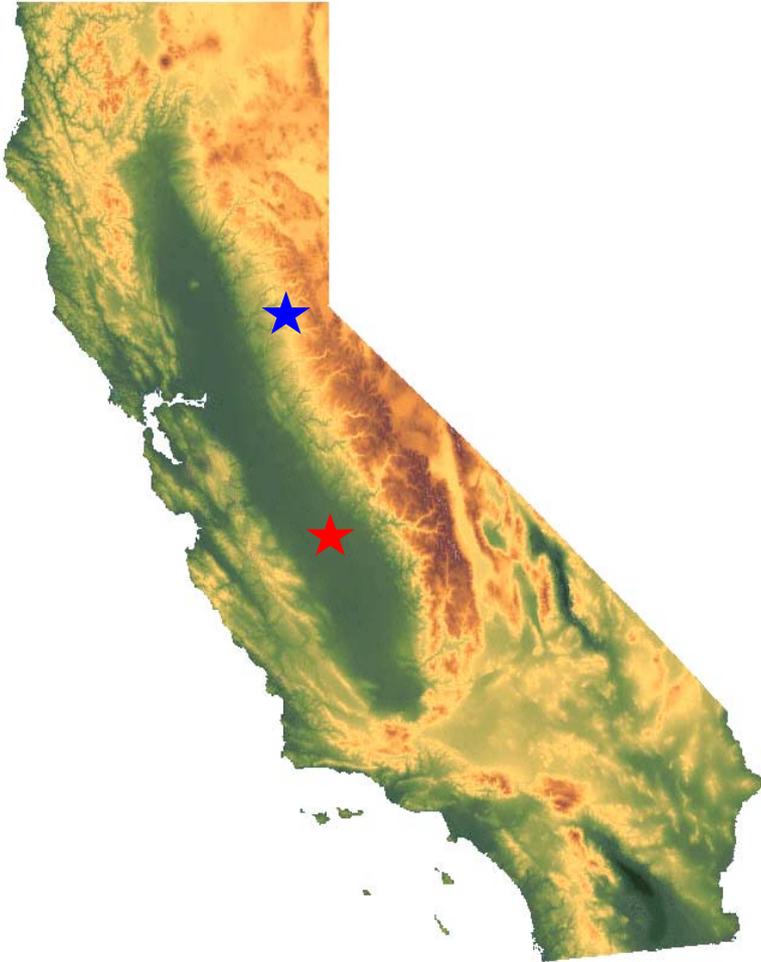
Characterization chemistry in the valley and an ini atmospheric che air basin



Ronald C. Cohen

A.H. Goldstein,
University of California, Berkeley
W.H. Brune, *Penn State*
Frank Keutsch, *U. of Wisc*
Joel Thornton, *U. of Wash.*
Paul Wennberg, *Caltech*

From the mountain to the valley



At the last Sacramento CALNEX meeting we proposed bringing the BEARPEX team to a site in the Southern SJV.

We are excited that ARB has helped us to make that happen.

BEARPEX Measurements 2007/2009

Unprecedented detail of the chemical composition, vertical gradients and fluxes of gases and aerosol

Mostly NSF sponsored team from CA, CO, PA, WI, OR, WA, and the UK

- Essentials: P, T, winds, NO, NO₂, CO, O₃, CO₂, etc.
- OH, HO₂, OH Lifetime
- 5 methods for NO_z
- Many organic acids
- Many peroxides
- 5 approaches to VOC (OVOC)
- H₂CO
- glyoxal
- new approaches to aerosol lifetime and composition



Outline

- Hypothesis & target questions
- Some background and example analyses; measurement capabilities
- Opportunities for enhancements

Hypothesis

The San Joaquin Valley of California is a region where secondary pollutants (O_3 and PM) will respond weakly or not at all to continued anthropogenic VOC controls while NO_x controls will be effective.

Questions to be addressed for SJV

- How well do we understand the sources of NO_x and VOC in the SJVAB?
- How well do we understand the coupling of HO_x, NO_x, O₃ and VOC photochemistry under conditions of VOC reactivity typical of the SJVAB?
- What happens to NO_x and VOC oxidation products at night? In the nocturnal boundary layer? In the residual layer? How does this chemistry affect NO_x, VOC, O₃ and aerosol production at night and on the following day?
- What factors affect the time scales for production and removal of 1st, 2nd, 3rd, etc. generation products of VOC and NO_x oxidation?
- How do these VOC reactions impact the photochemical production and loss of ozone, OH, NO_y species, and aerosols?

Questions to be addressed in collaboration with partners

- Are there significant differences in precursors or ozone formation chemistry between the Central Valley and South Coast Air Basin?
- Will precursor differences between the Central Valley and the South Coast Air Basin lead to different chemical transformation processes and different responses to emissions reductions?
- What is the importance of natural emissions to the ozone formation process? Are there regional differences in the formation rates and efficiency for particulate matter as well?

Tasks—Emissions & $\text{HO}_x/\text{NO}_x/\text{O}_3$ Chemistry

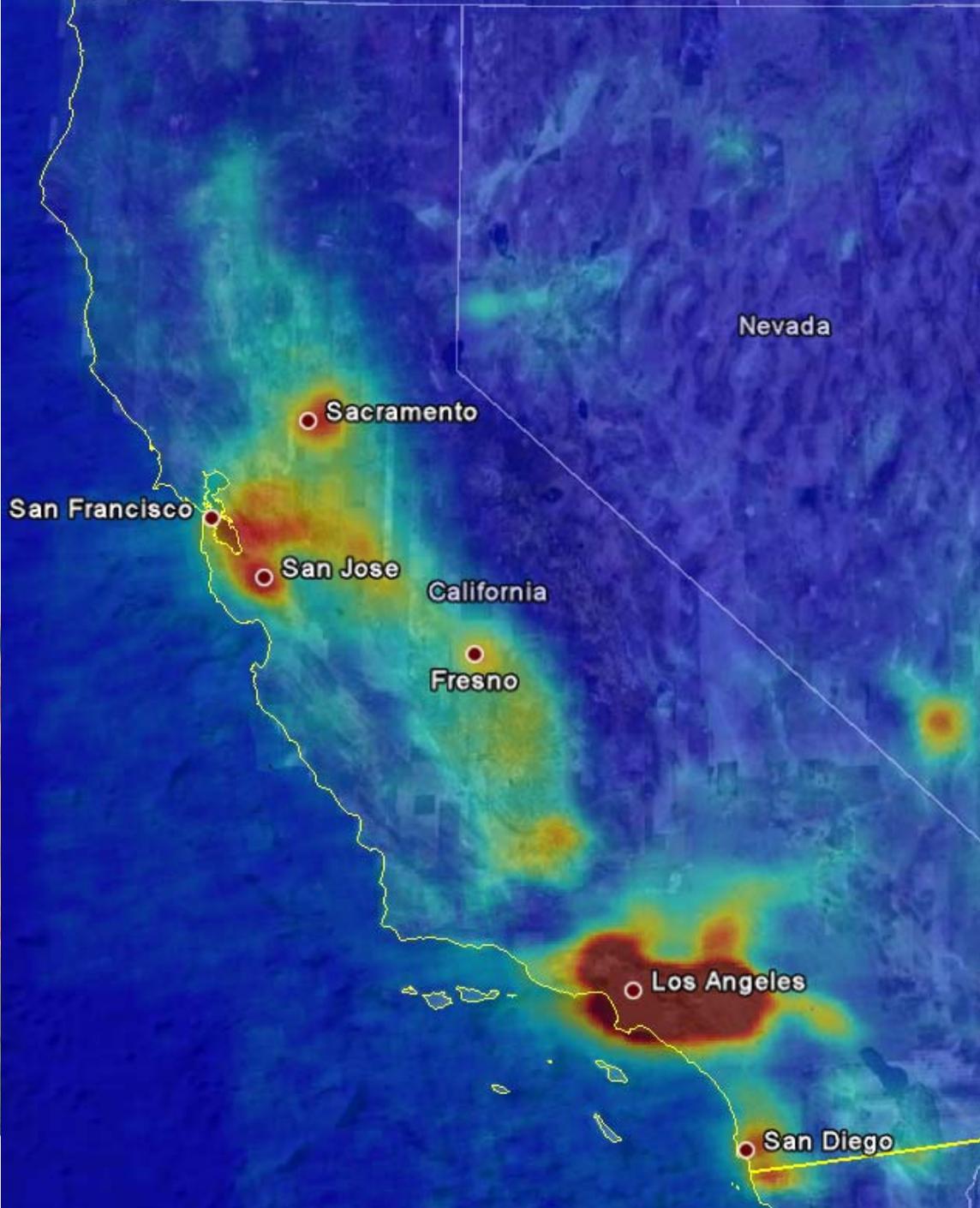
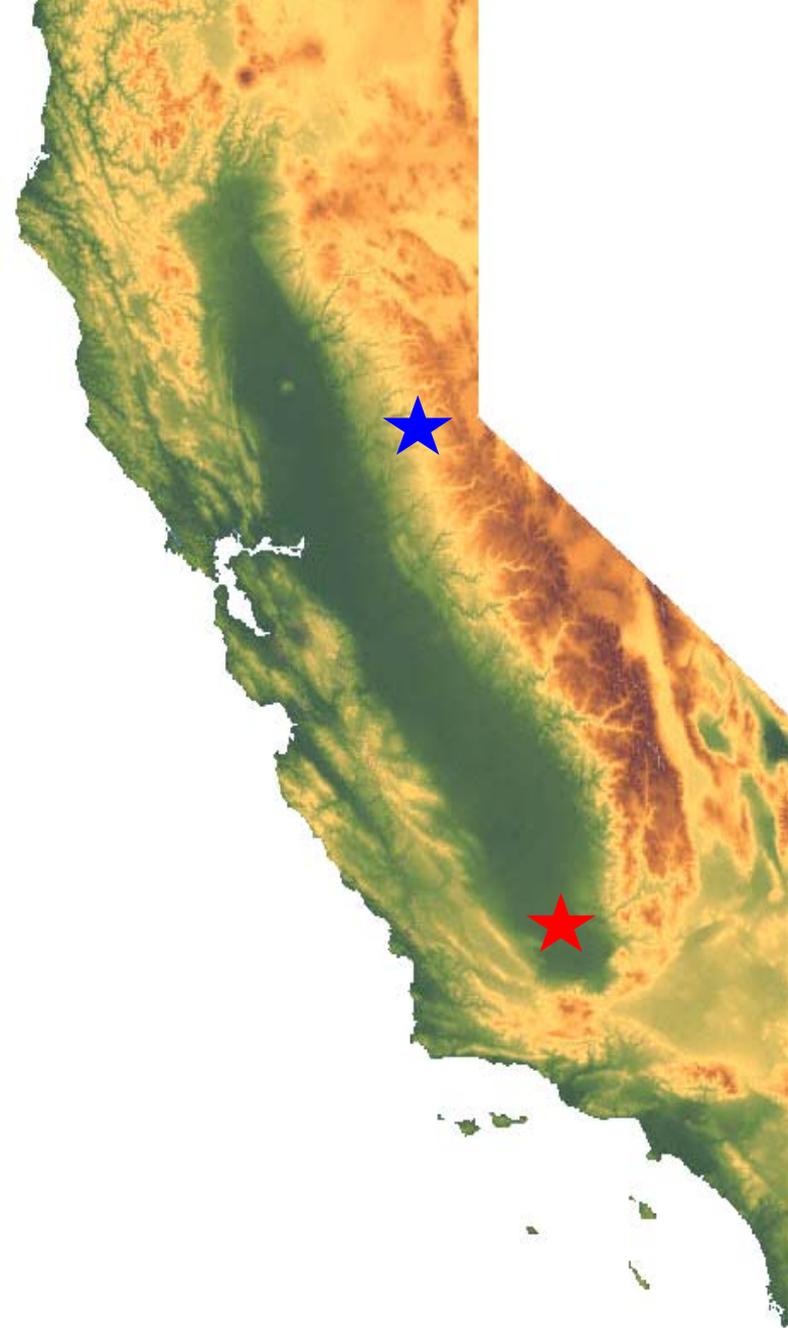
- evaluate how O_x , OH and HO_x respond to changes in NO_x at the SJV field site
- assess the sources of OH reactivity in the region comparing total OH loss with the sum of OH losses calculated from observed organics and nitrogen oxides
- compare mechanisms for production and removal of HO_x that are important to indicator formulations (HOOH and HNO_3), compare these ideas to instantaneous evaluations of ozone production rate models (e.g. Thornton et al. 2002, Spencer et al. 2009) that use HO_2NO_2 , peroxide, organic nitrate and HNO_3 production rates as tests of sensitivity to changes in NO_x and then assess the chemical regime based on these combined indicators
- evaluate the NO_x budget including sources and sinks

Tasks--Biogenics

- evaluate the role of biogenic chemistry in ozone production emphasizing HO_x recycling and organic nitrates
- we will calculate the SOA production rate from the observed organics including both α -dicarbonyls and highly oxidized VOC
- Assess the the role of biogenic VOC in the sequestration of NO_x as PAN like molecules and evaluate effect on O₃. We will compare and contrast our SJVAB observations with those at other CalNex sites and those from BEARPEX-2007 and 2009 in a rural NO_x-limited forest
- Perform source attribution studies using positive matrix factorization e.g. Lamanna and Goldstein, 1999; Goldstein et al., 2008) for the broad suite of VOC measured, to assess the relative importance of biogenic versus anthropogenic sources, and specific types of anthropogenic sources, affecting air quality in the region.

Background and Example Analyses: Emissions



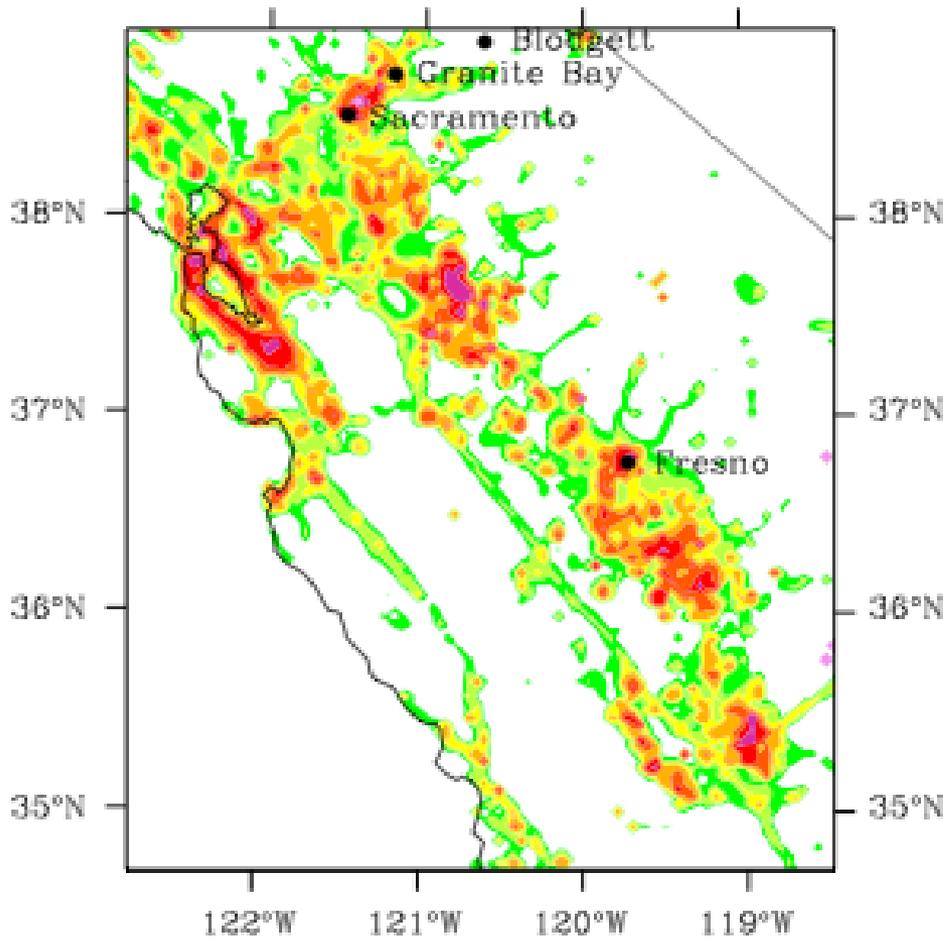


Anthropogenic VOC

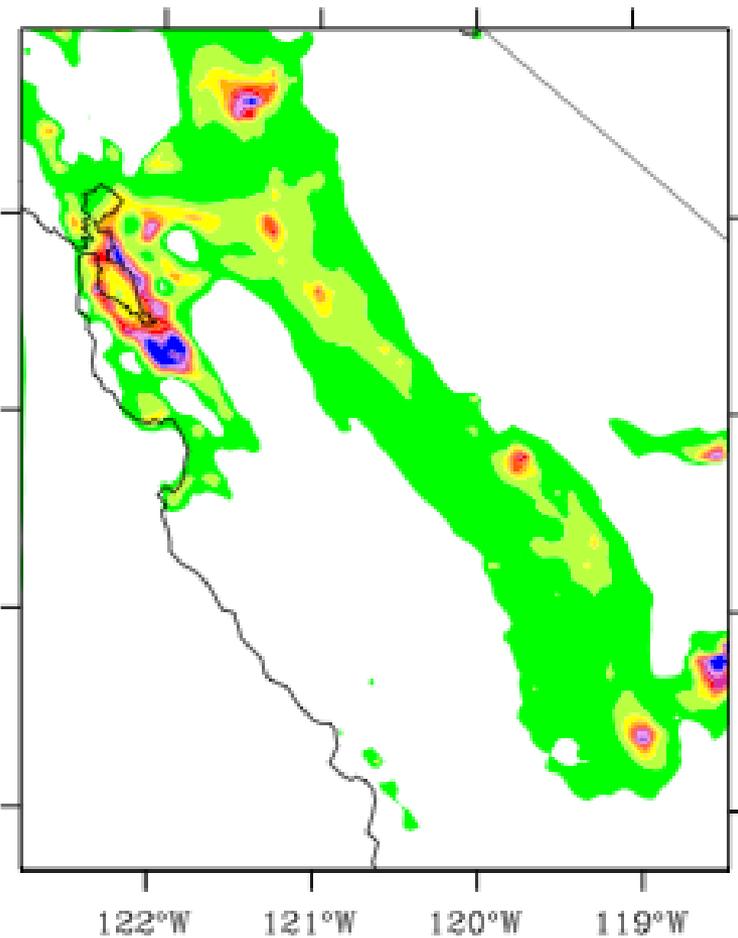
Steiner et al 2007

Emissions

R_{VOC}



mol s^{-1}



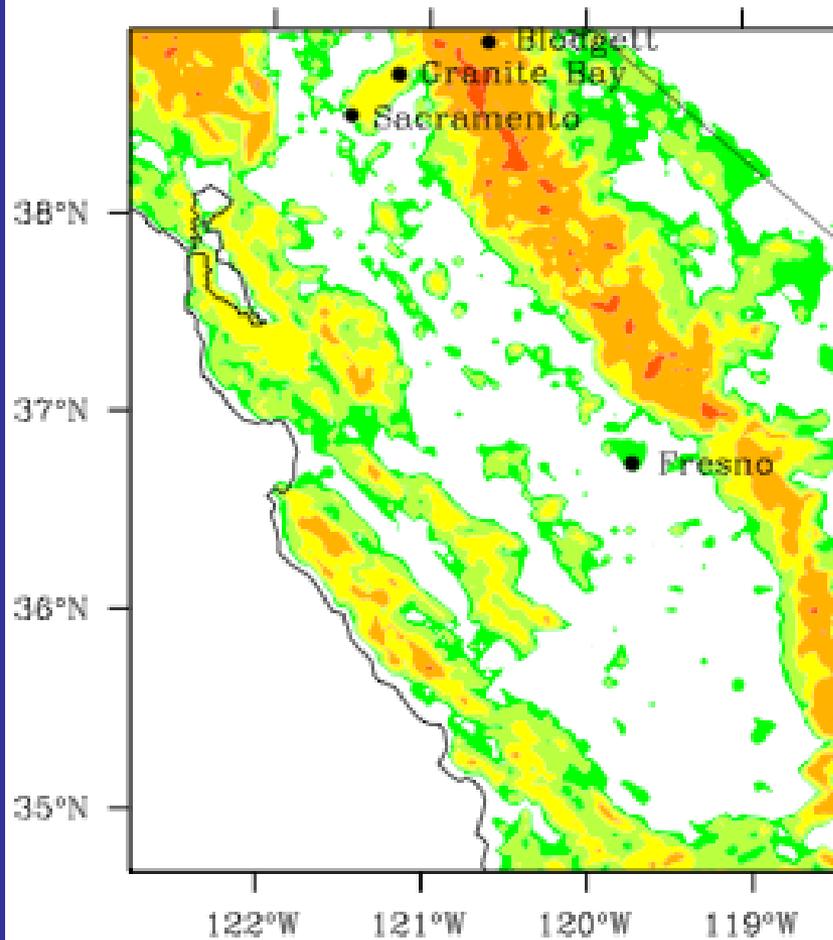
s^{-1}

Biogenic VOC

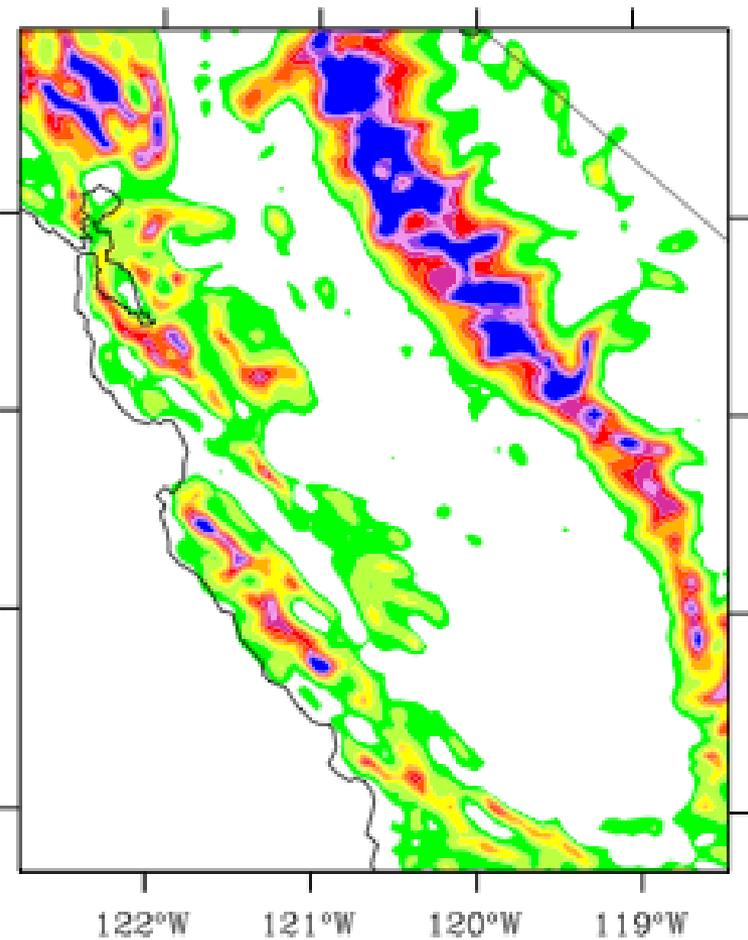
Steiner et al 2007

Emissions

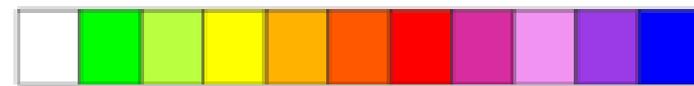
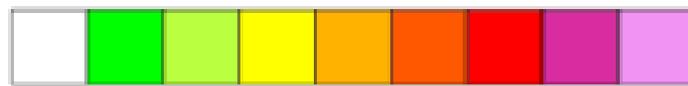
R_{VOC}



mol s⁻¹



s⁻¹



Total OH reactivity: Model and summed from VOC and NO_x Obs



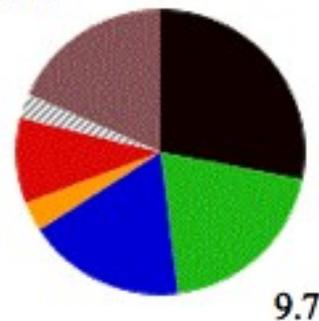
A) AM Sacramento

Fresno

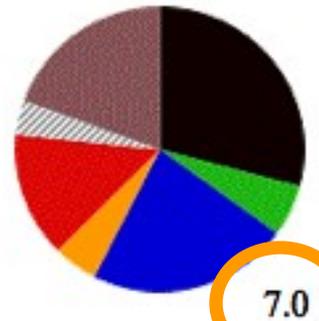
Granite Bay

Blodgett

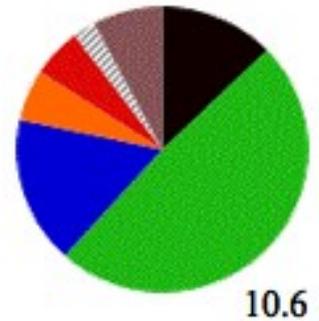
Modeled



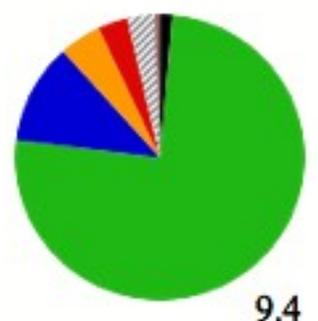
9.7



7.0



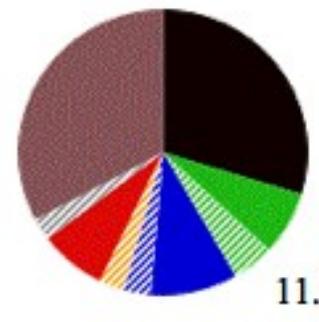
10.6



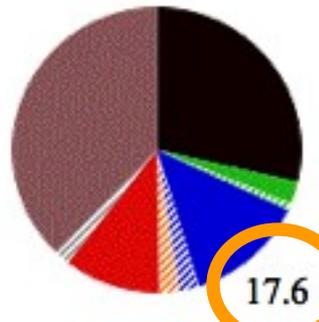
9.4

- AVOC
- BVOC
- ALD
- OXVOC
- CO
- CH4
- NO2

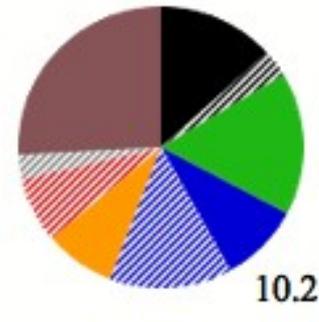
Measured



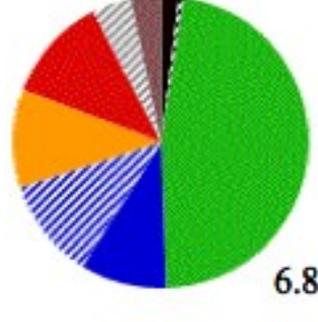
11.5



17.6

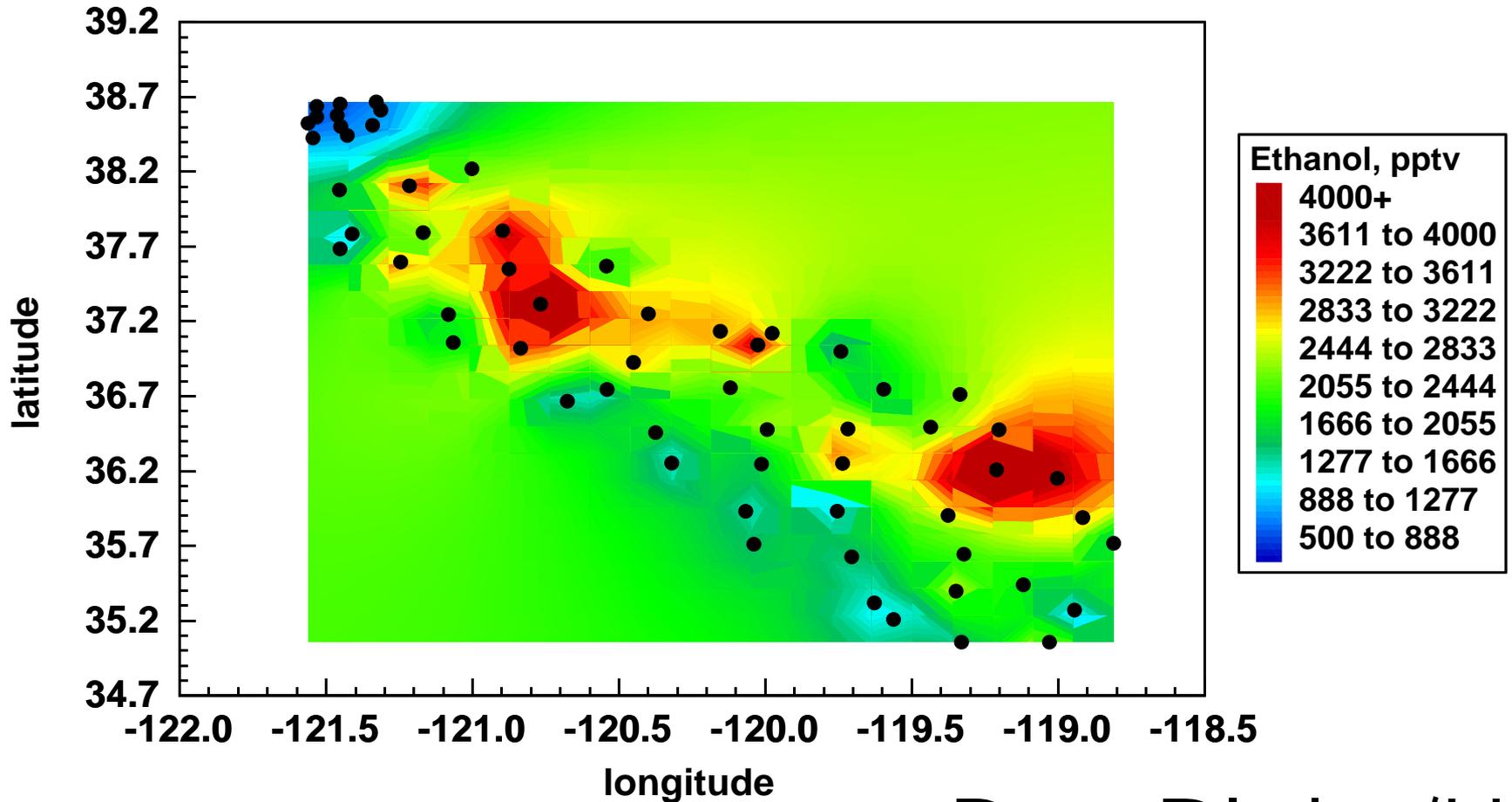


10.2



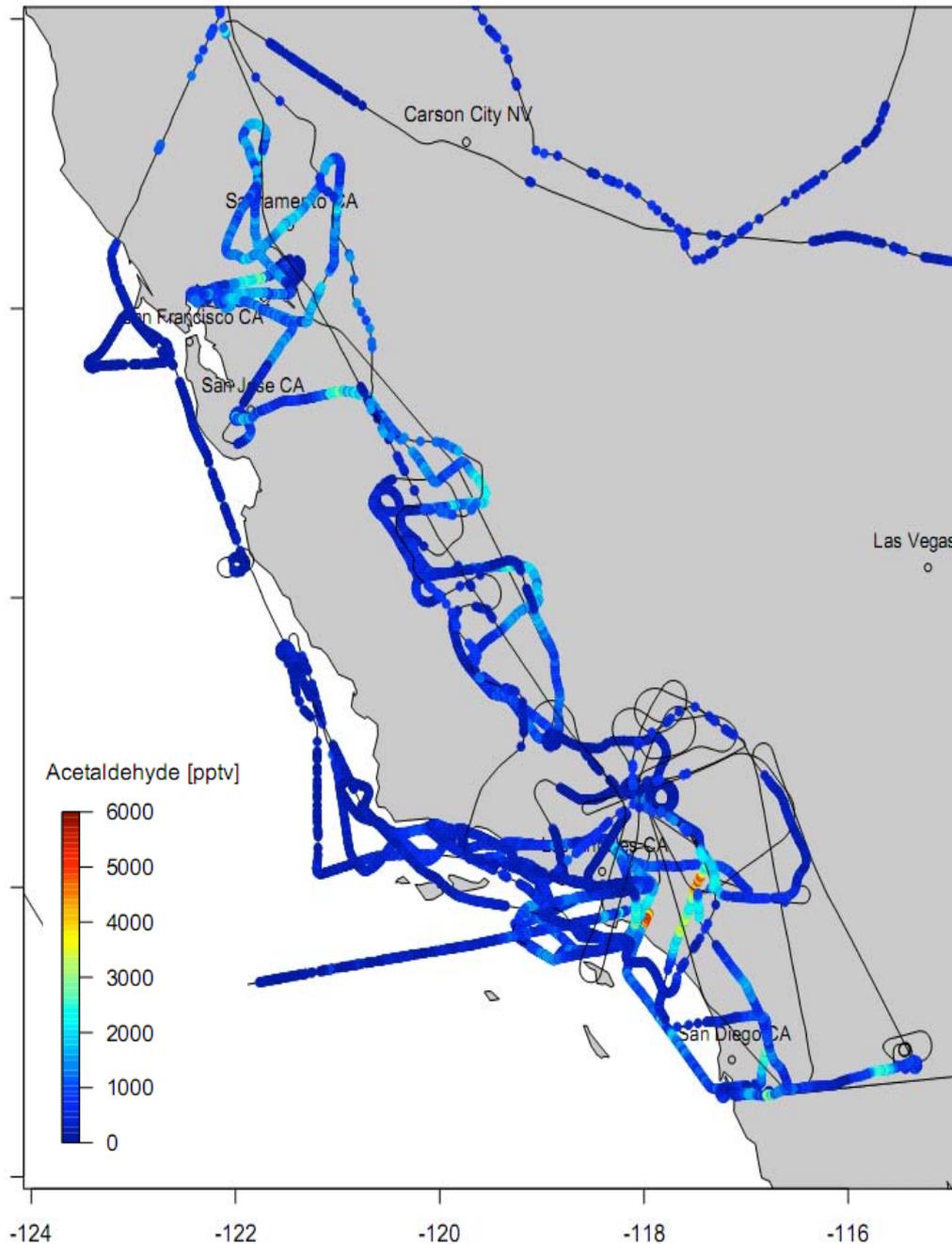
6.8

VOC emissions from dairies in the California Central Valley and their impact on local and regional ozone - Yang et al.



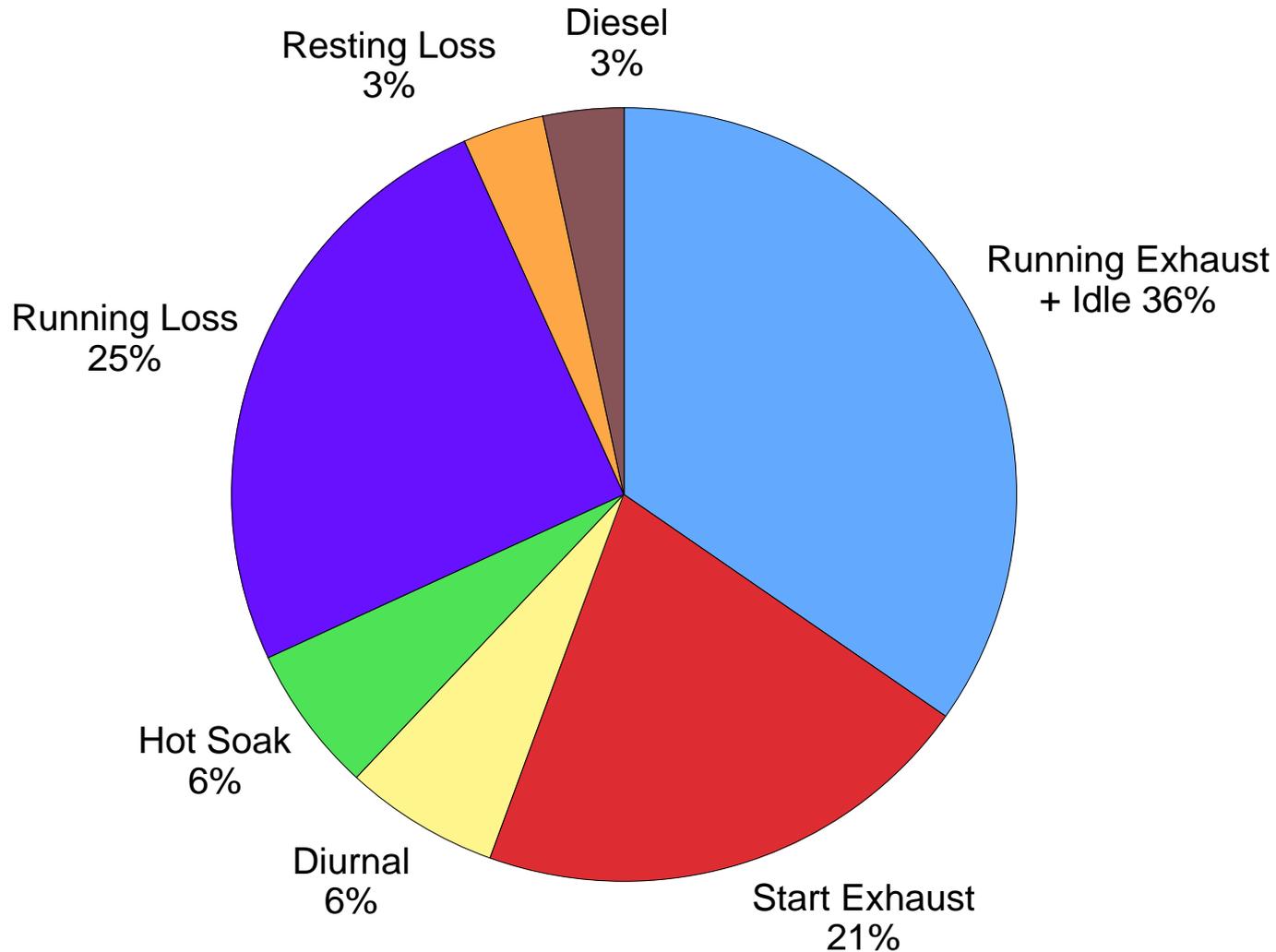
Don Blake/UCI

Acetaldehyde



Armin
Wisthaler,
Univ
Innsbruck

Motor Vehicle VOC Emissions



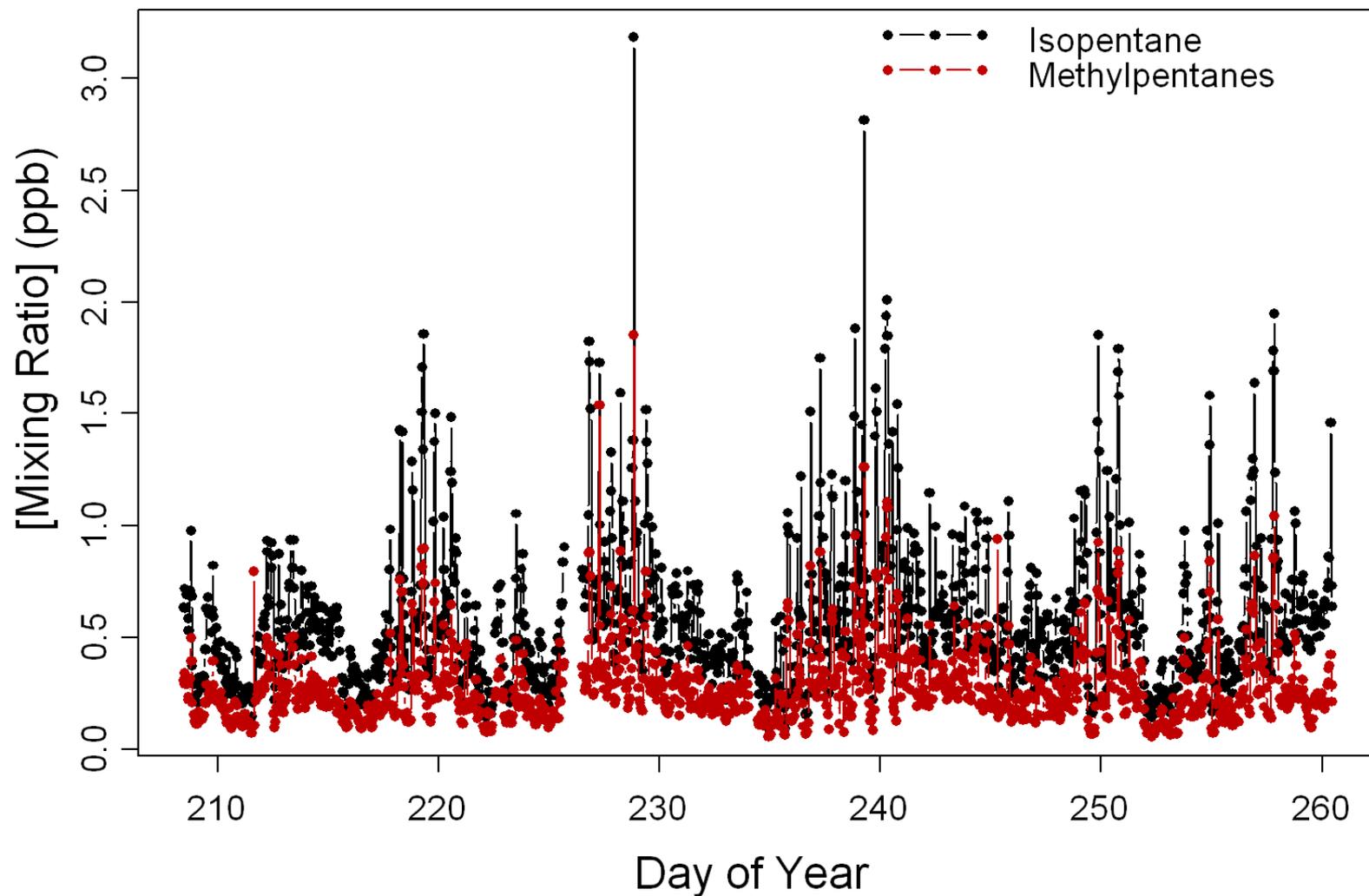
California EMFAC model predictions for Sacramento in summer 2001

Exhaust vs. Evaporative VOC

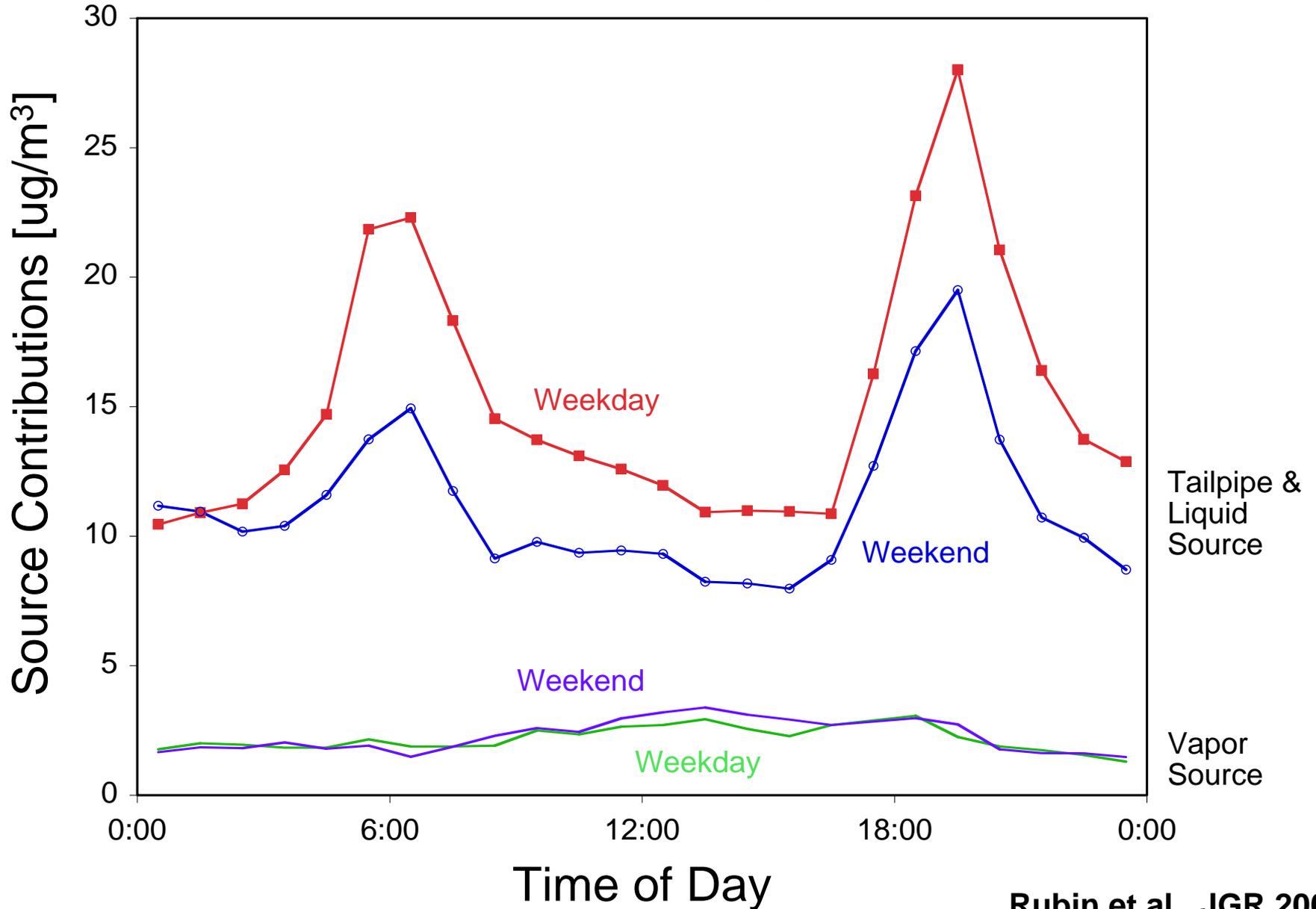
Isopentane & methylpentanes are:

- abundant in gasoline (7.5 and 5.8 wt%)
 - not very reactive in the atmosphere
-
- Isopentane greatly enriched in vapor emissions relative to methylpentanes
 - 27 vs. 6.5 wt% in vapor

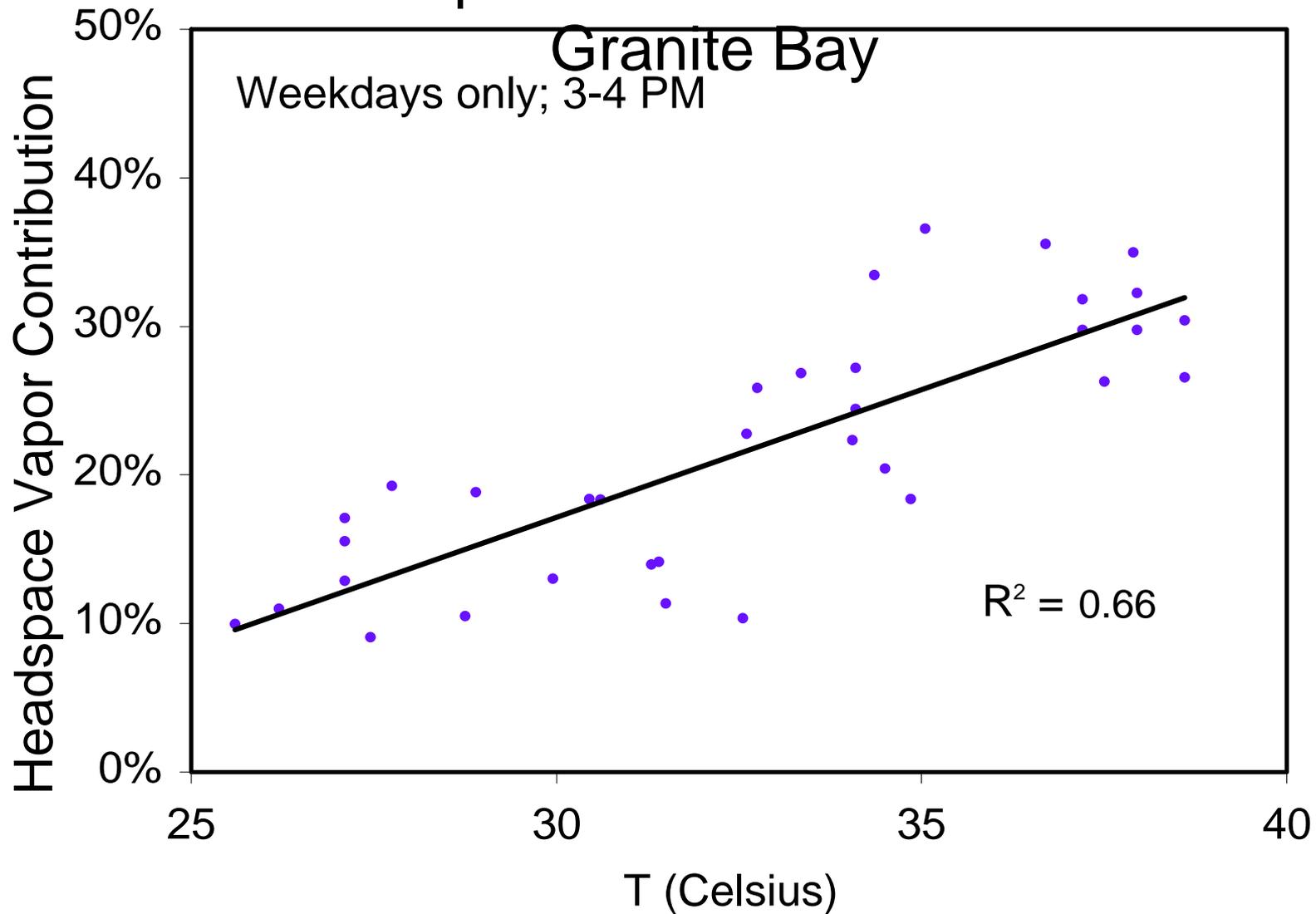
Granite Bay: 18 July - 15 Sept 2001

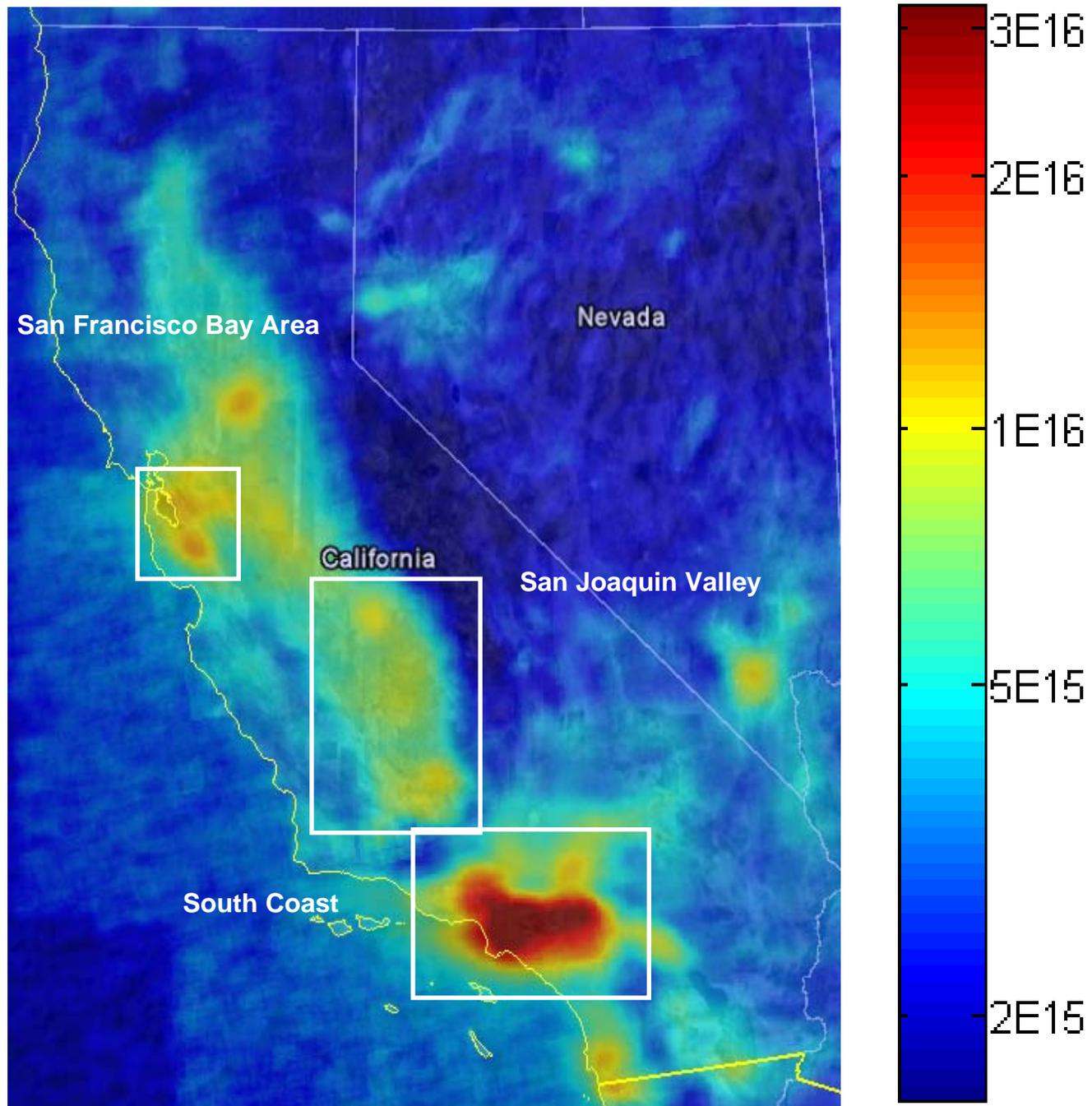


Chemical Mass Balance Results Granite Bay

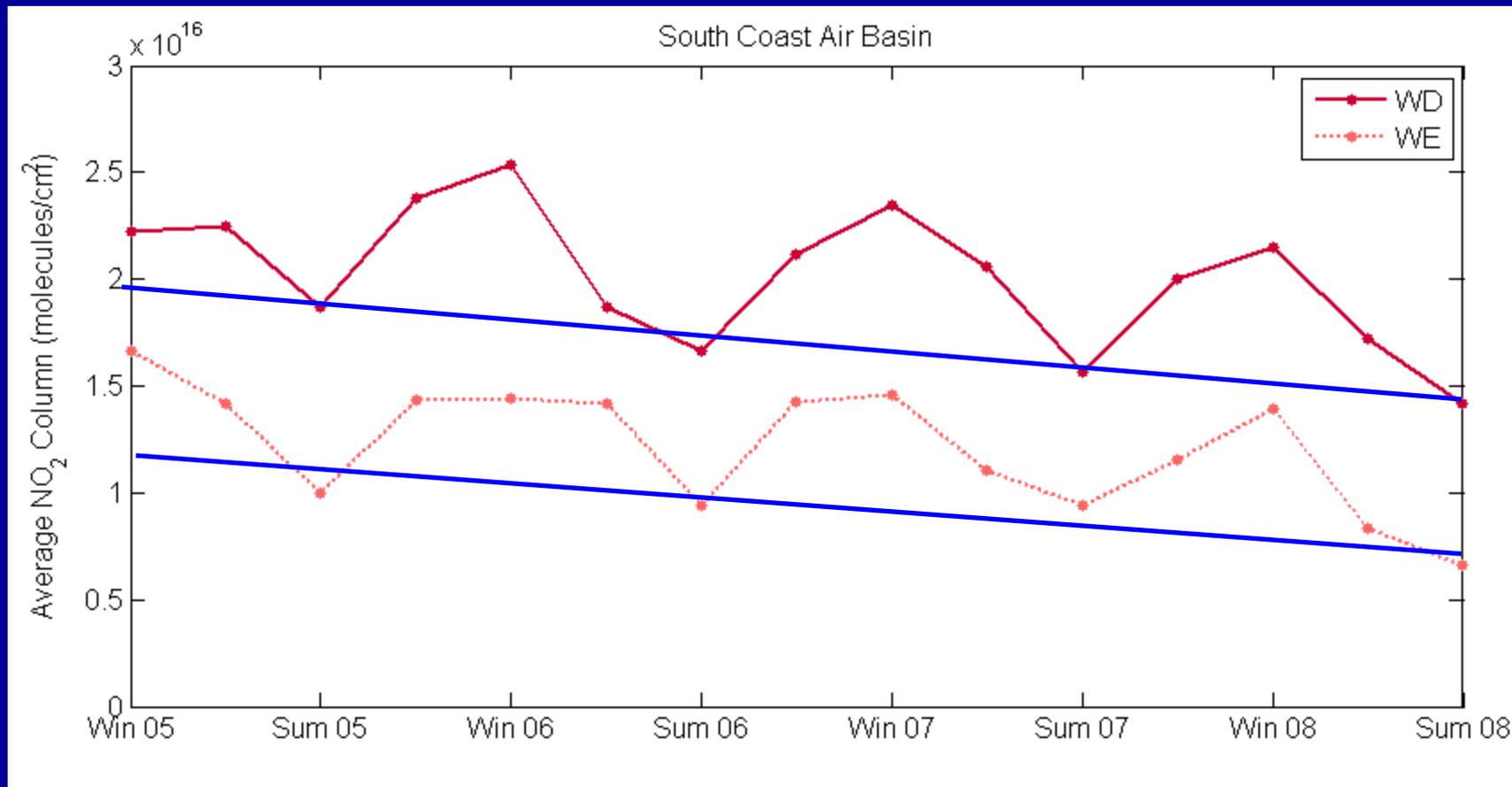


Vapor Contribution vs. T

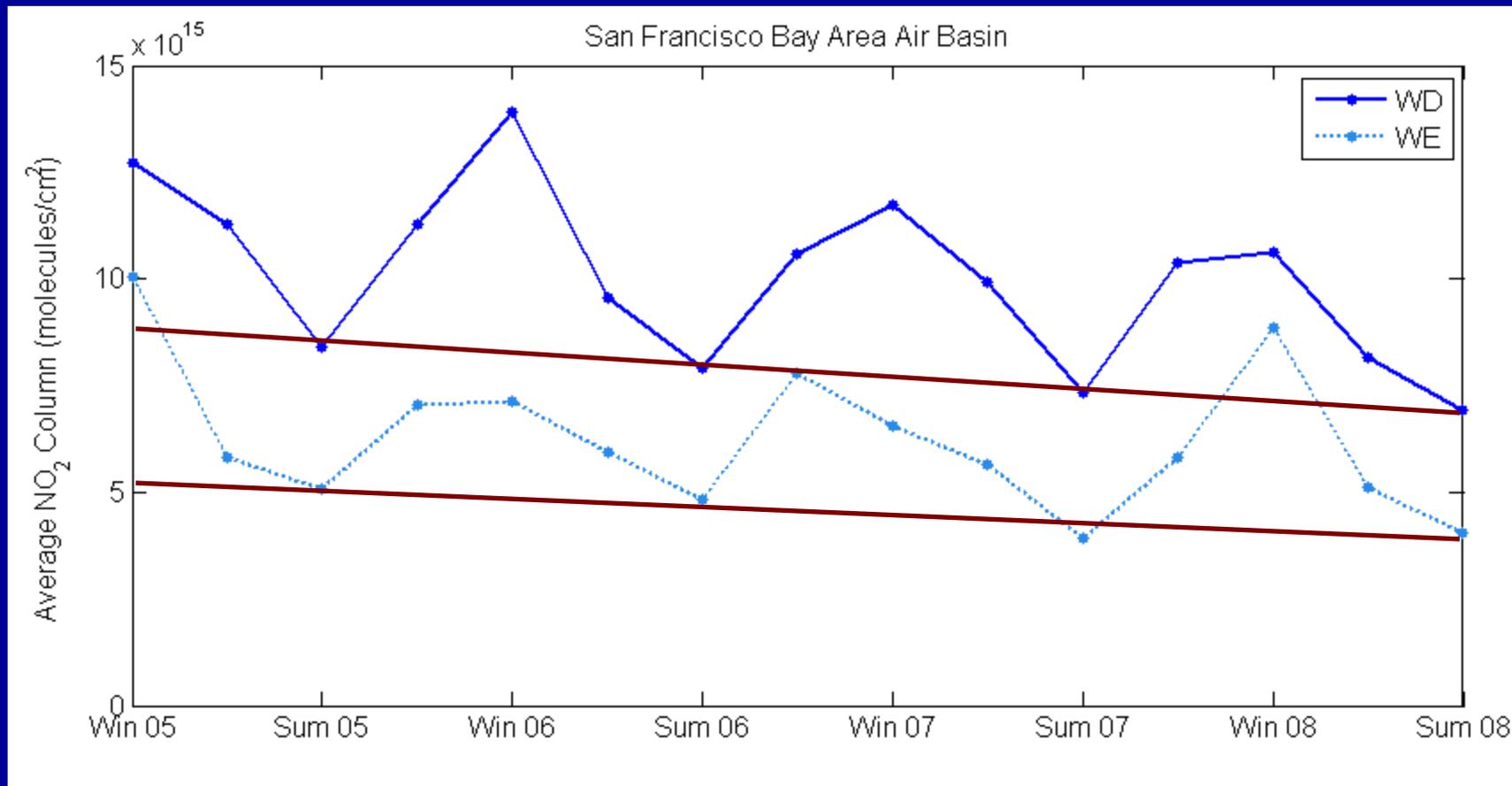




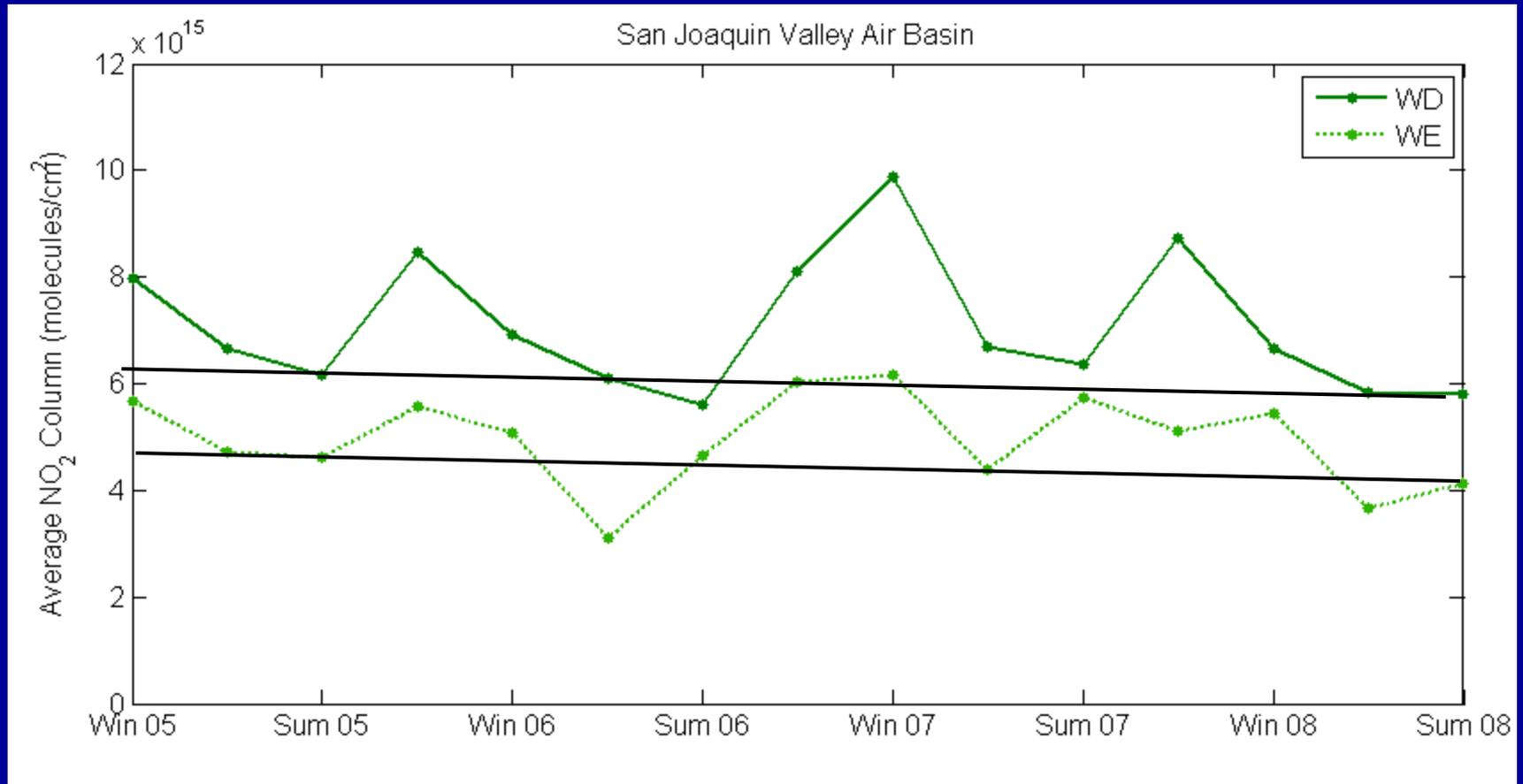
~8%/yr decrease in NO_x
weekdays and weekends



San Francisco 5%/yr decrease

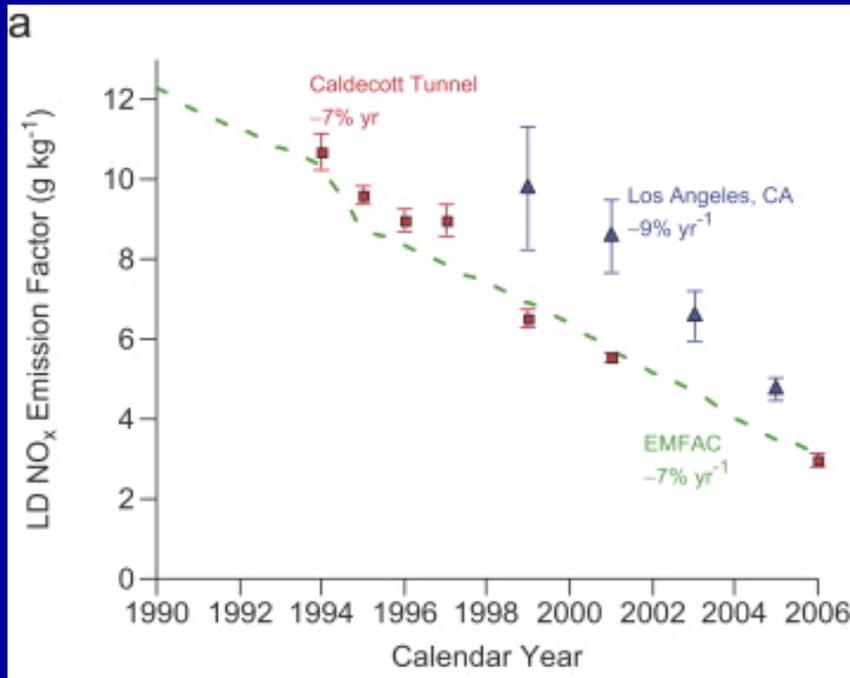


San Joaquin Valley: Decrease not detectable

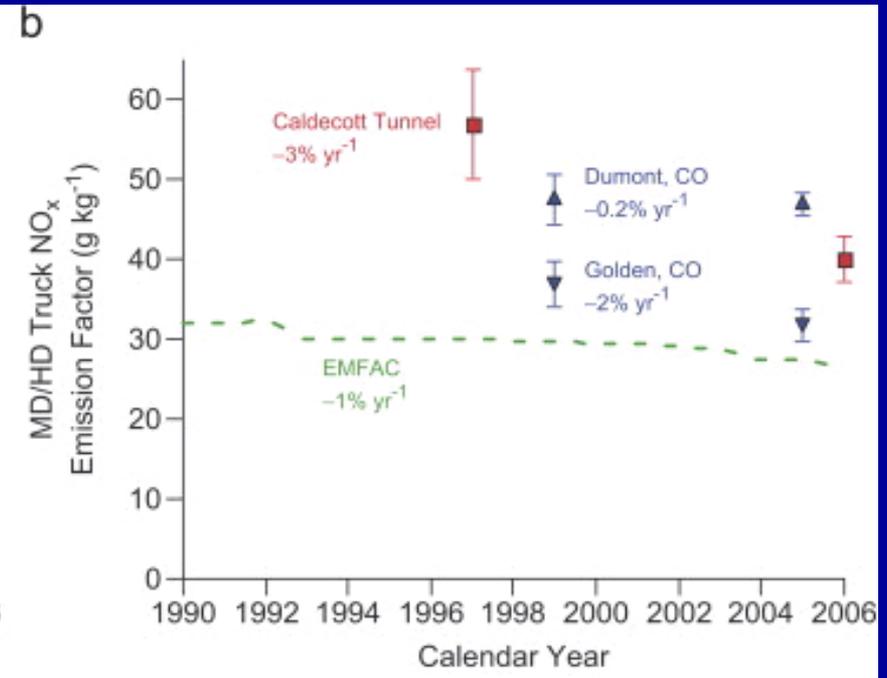


Caldecott Tunnel study of NO_x emission factors

Light Duty Vehicles

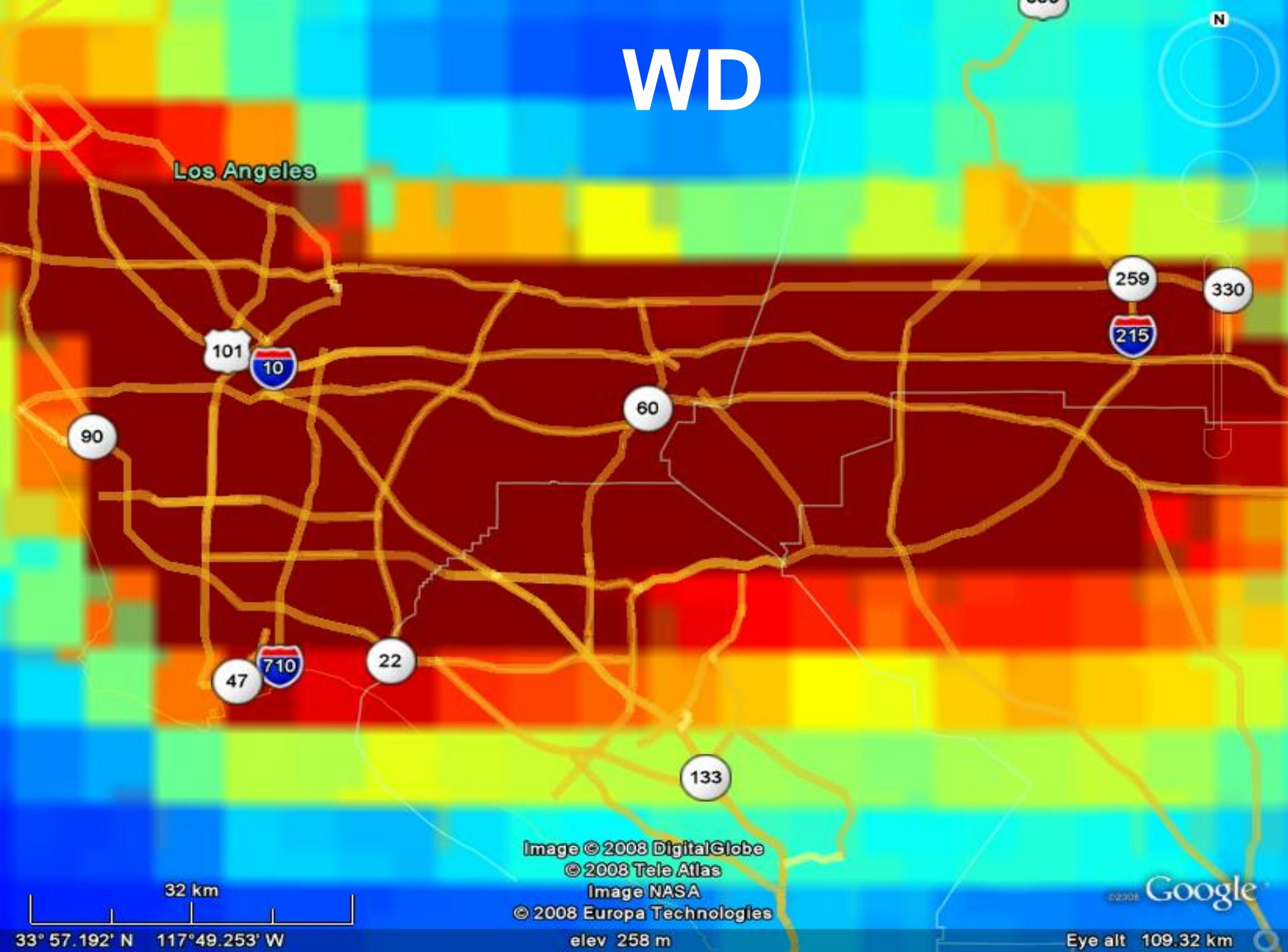


Medium/Heavy Duty Vehicles



WD

Los Angeles



WE

Los Angeles

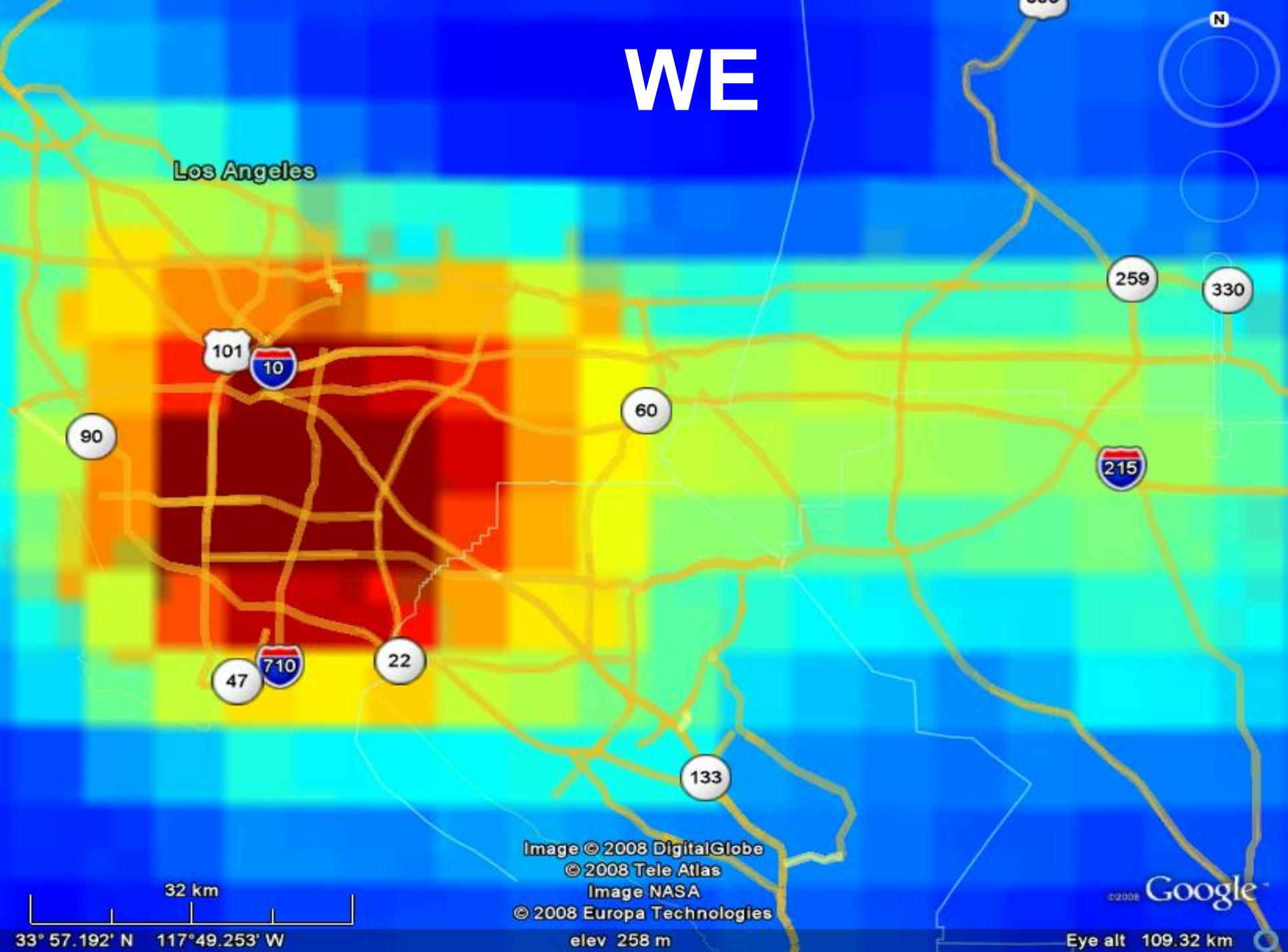


Image © 2008 DigitalGlobe
© 2008 Tele Atlas
Image NASA
© 2008 Europa Technologies

©2008 Google

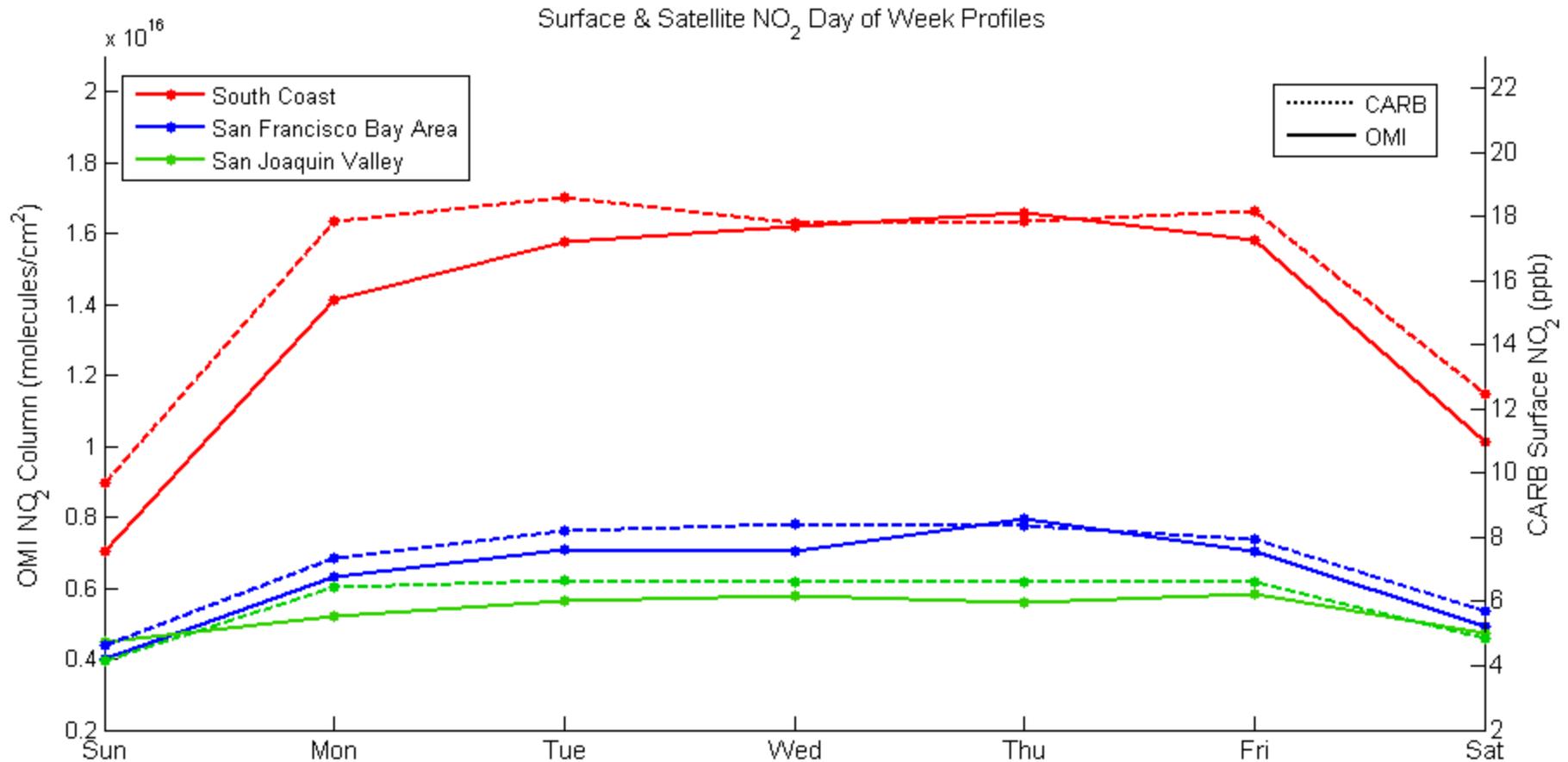
32 km

33° 57.192' N 117° 49.253' W

elev 258 m

Eye alt 109.32 km

Day of Week Profiles: OMI & CARB



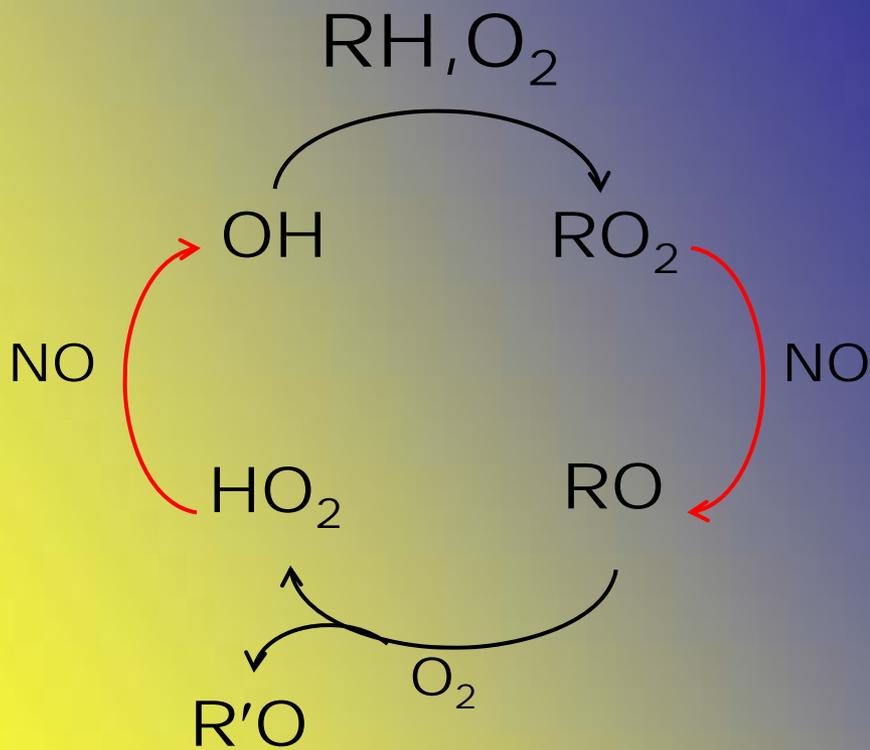
Data averaged for Jun-Aug 2004 - 2007

Background and Example Analyses: Chemistry

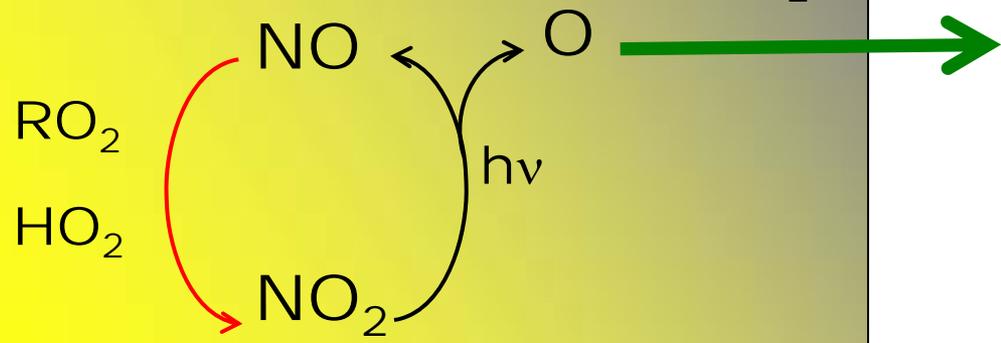


Catalytic Cycles

HO_x Cycle

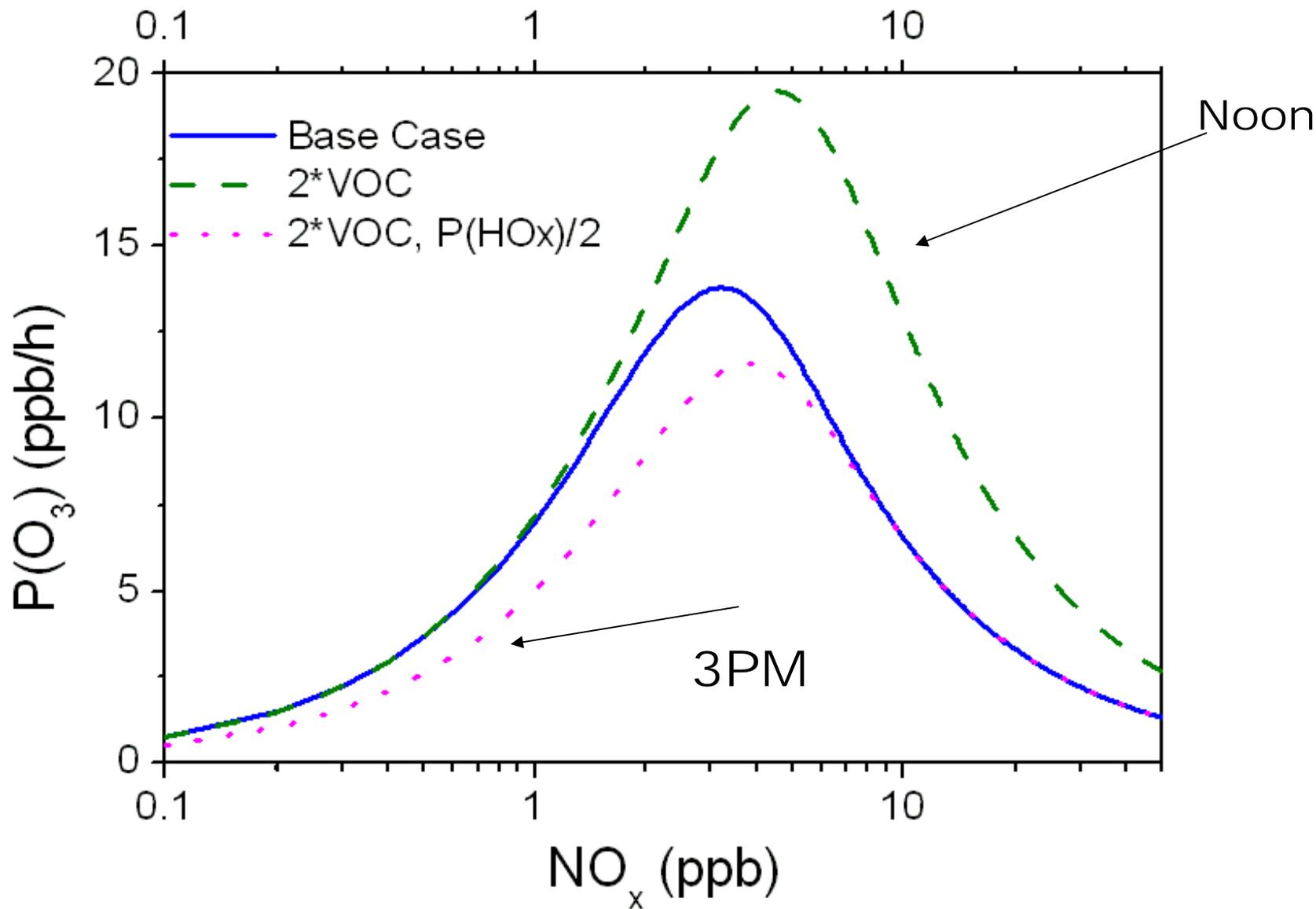


NO_x Cycle

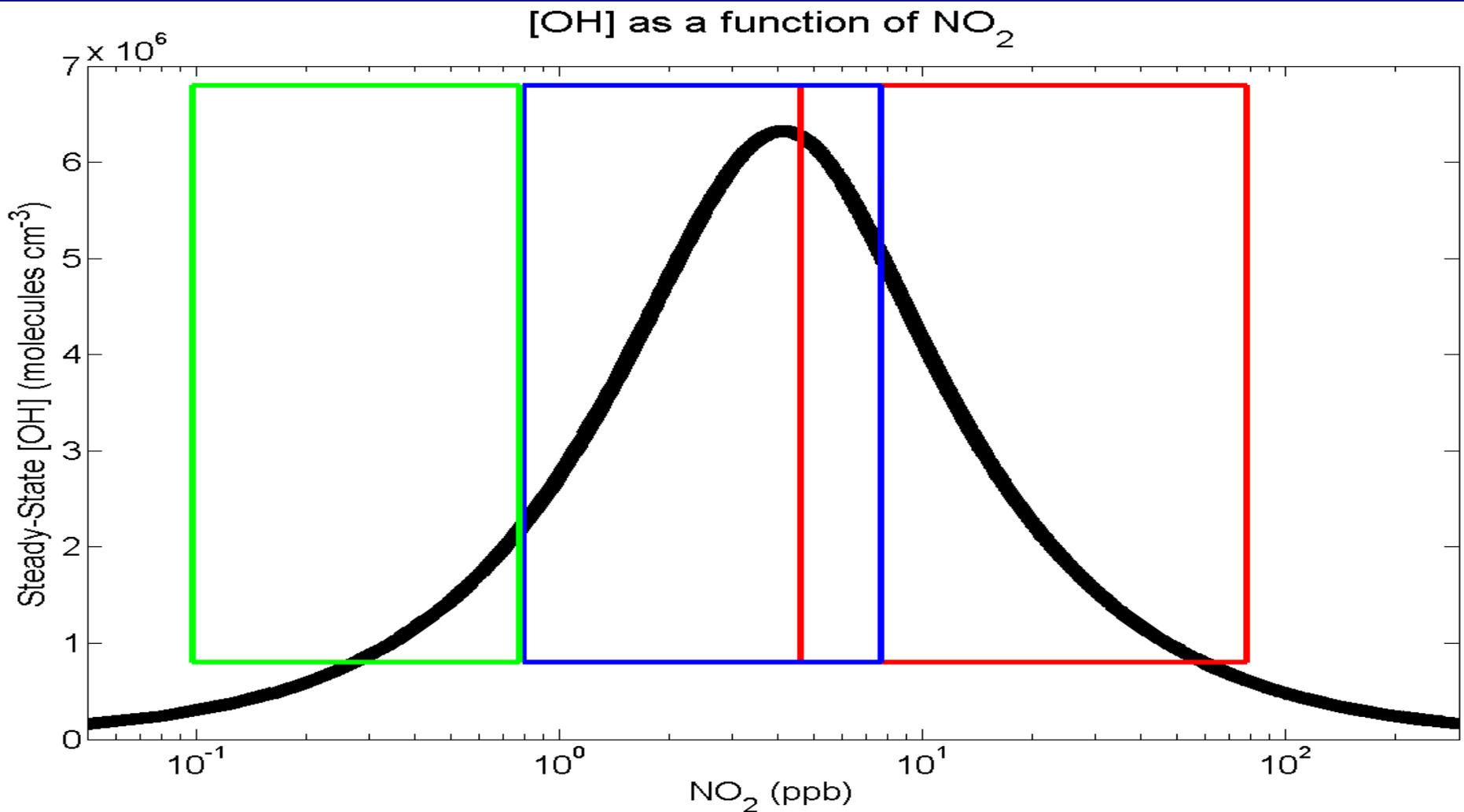


O₃

Photochemical Ozone Production NO_x , VOC Reactivity, HO_x production



NO_x and OH

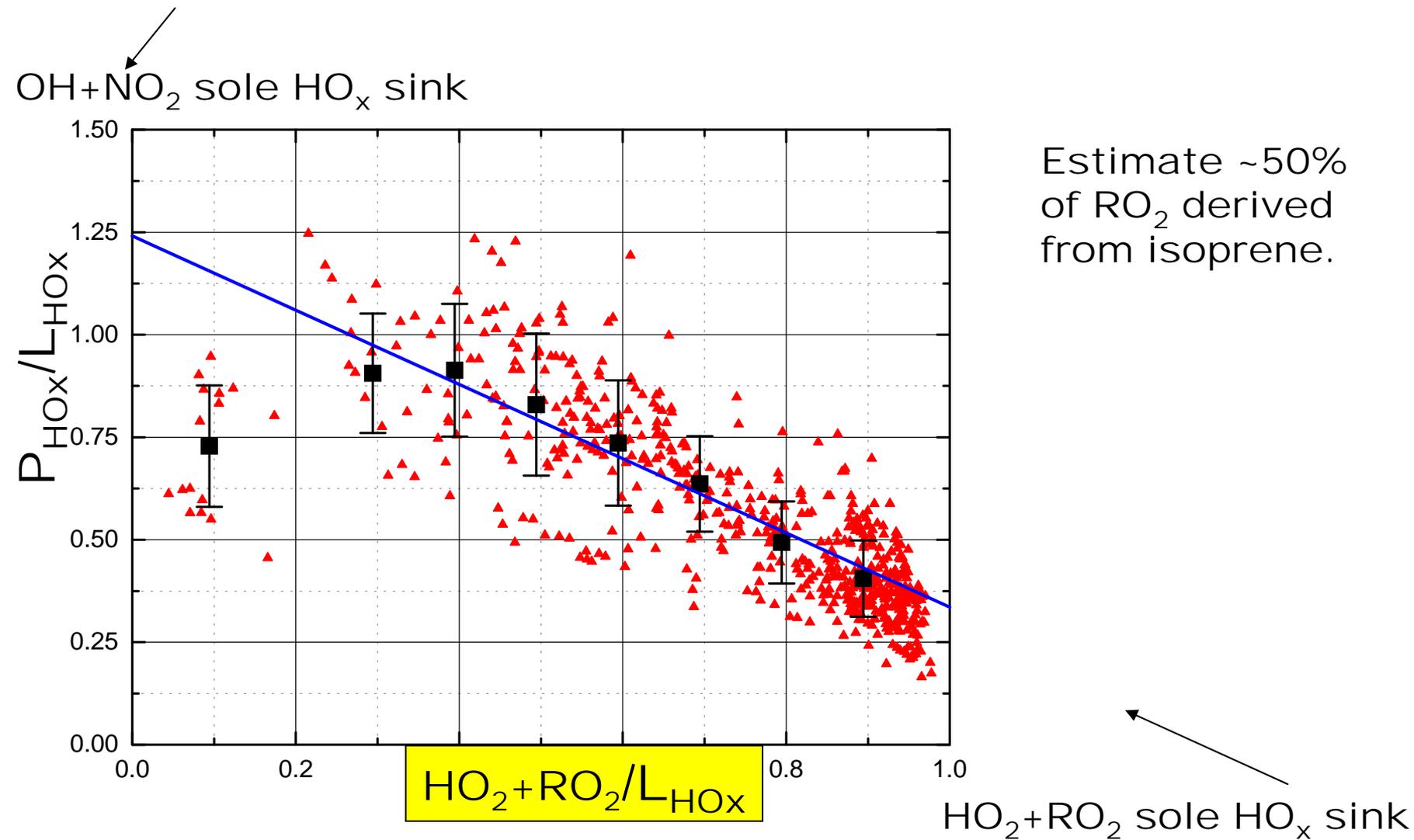


Do we understand OH/HO₂/RO₂ chemistry?

The answer is no at high NO_x and at high isoprene levels.

That means all models have incorrect ozone production rates under these conditions.

Thornton et al. 2002



Implication: RO₂ + HO₂ not understood

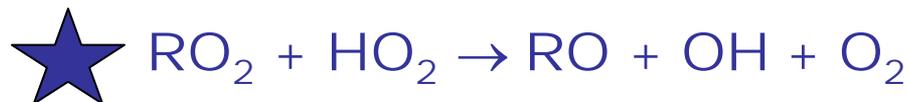
In 2002 we suggested that the products of RO₂ + HO₂ are mostly (90%) chain carriers not chain terminators, for example



Result at least partly confirmed in the lab and by 4 different groups measuring OH/HO₂ and RO₂.

At high isoprene OH + isoprene has the effect of increasing the HO_x source by much more than the effect of the H₂CO produced.

RO₂ + HO₂ recycles OH



Hasson, Tyndall and Orlando J. Phys. Chem. A 108 5979, 2004
also Jenkin et al. 2007 and Dillon and Crowley 2008

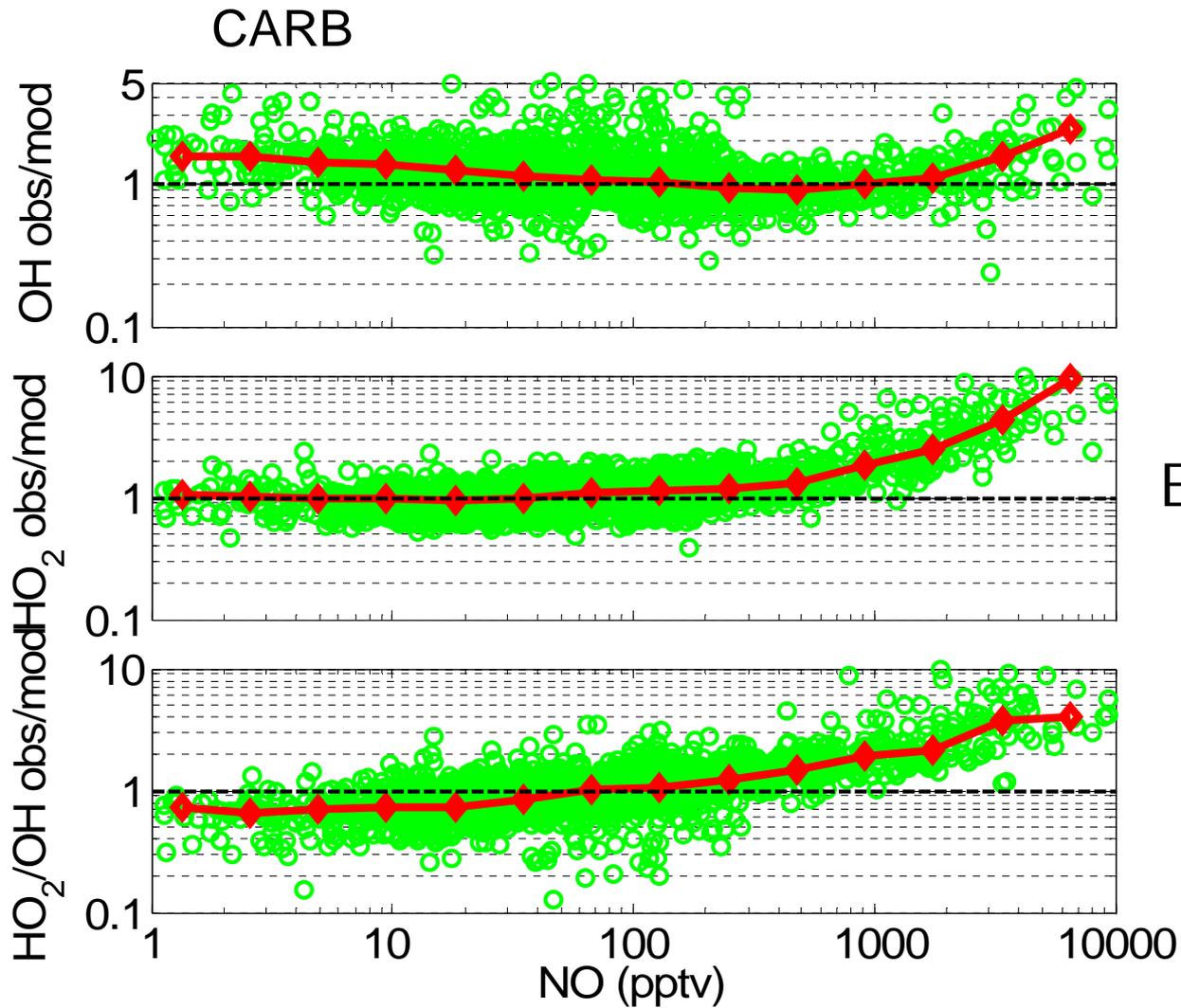
For oxygenated RO₂ radicals + HO₂ (~30-50% OH yields)

Consistent with direct measurements of OH by Penn State (Brune). Mainz (Lelieveld) groups and more recently Juelich and NCAR.

OH much larger than predicted when isoprene is high.

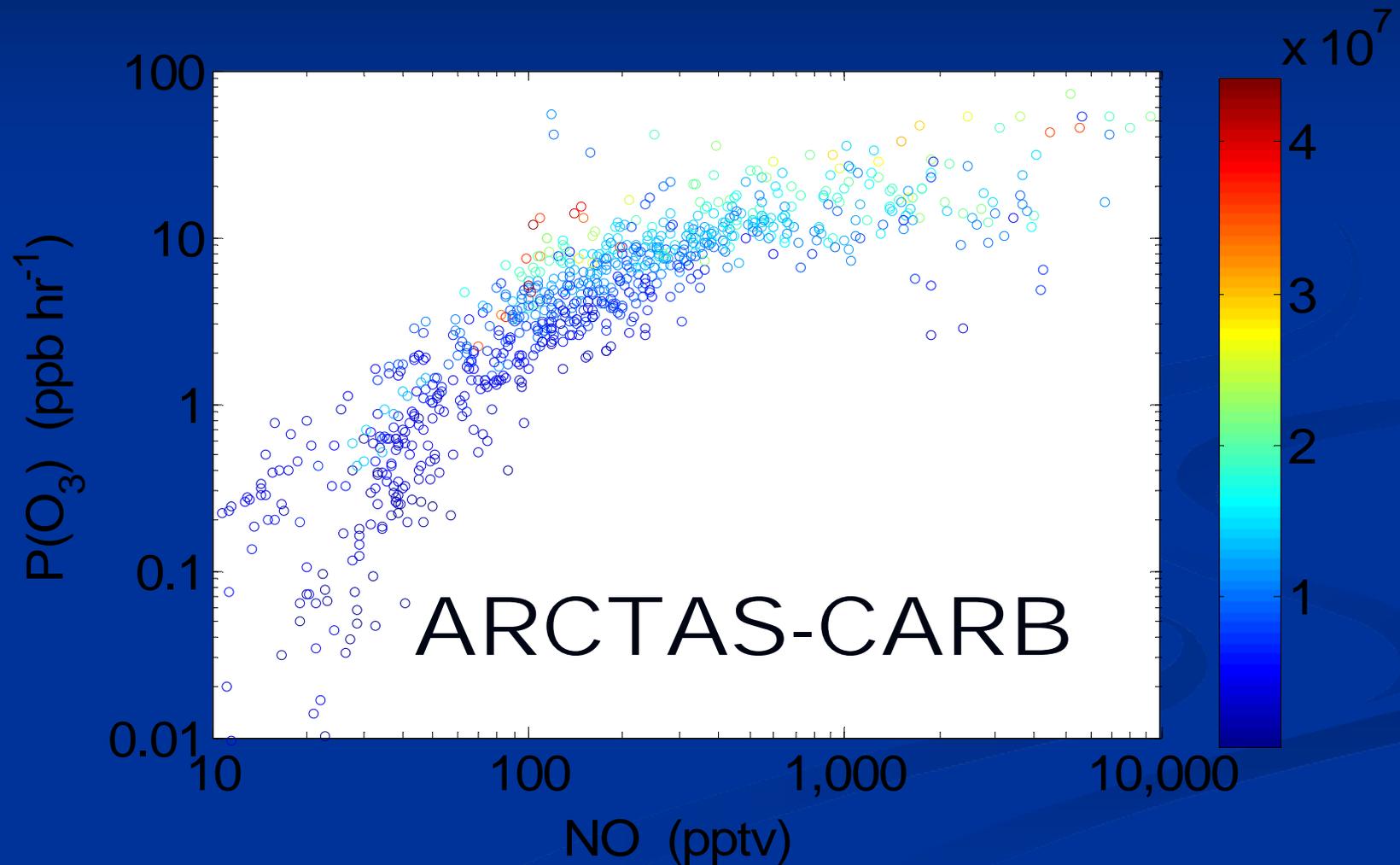
Some analyses suggest isoprene oxidation products amplify HO_x increasing it by more than the reaction above would indicate.

HO_x Chemistry during ARB-ARCTAS



Brune et al.

Implication: O_3 production is faster than in our models at high NO_x and at high isoprene

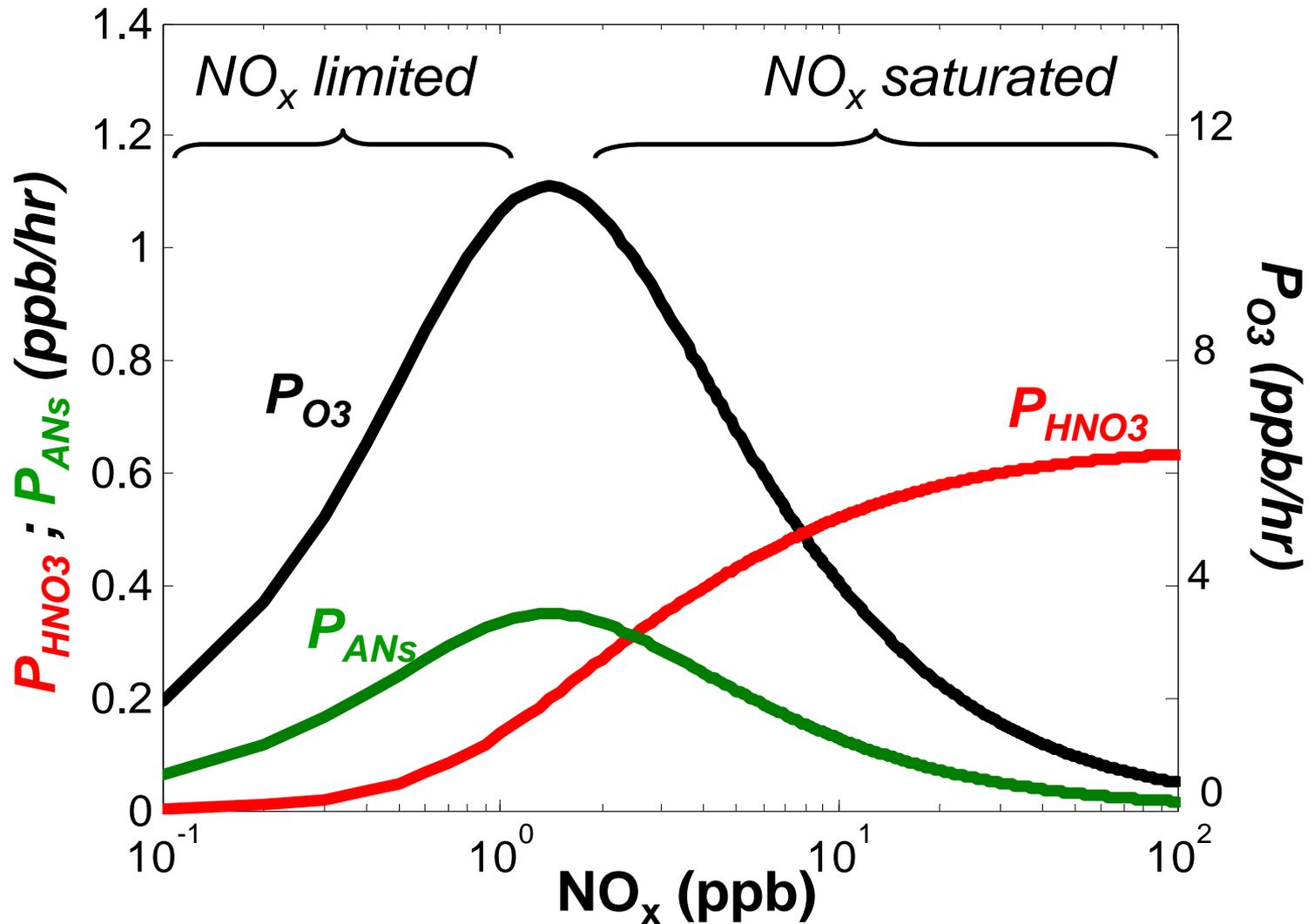


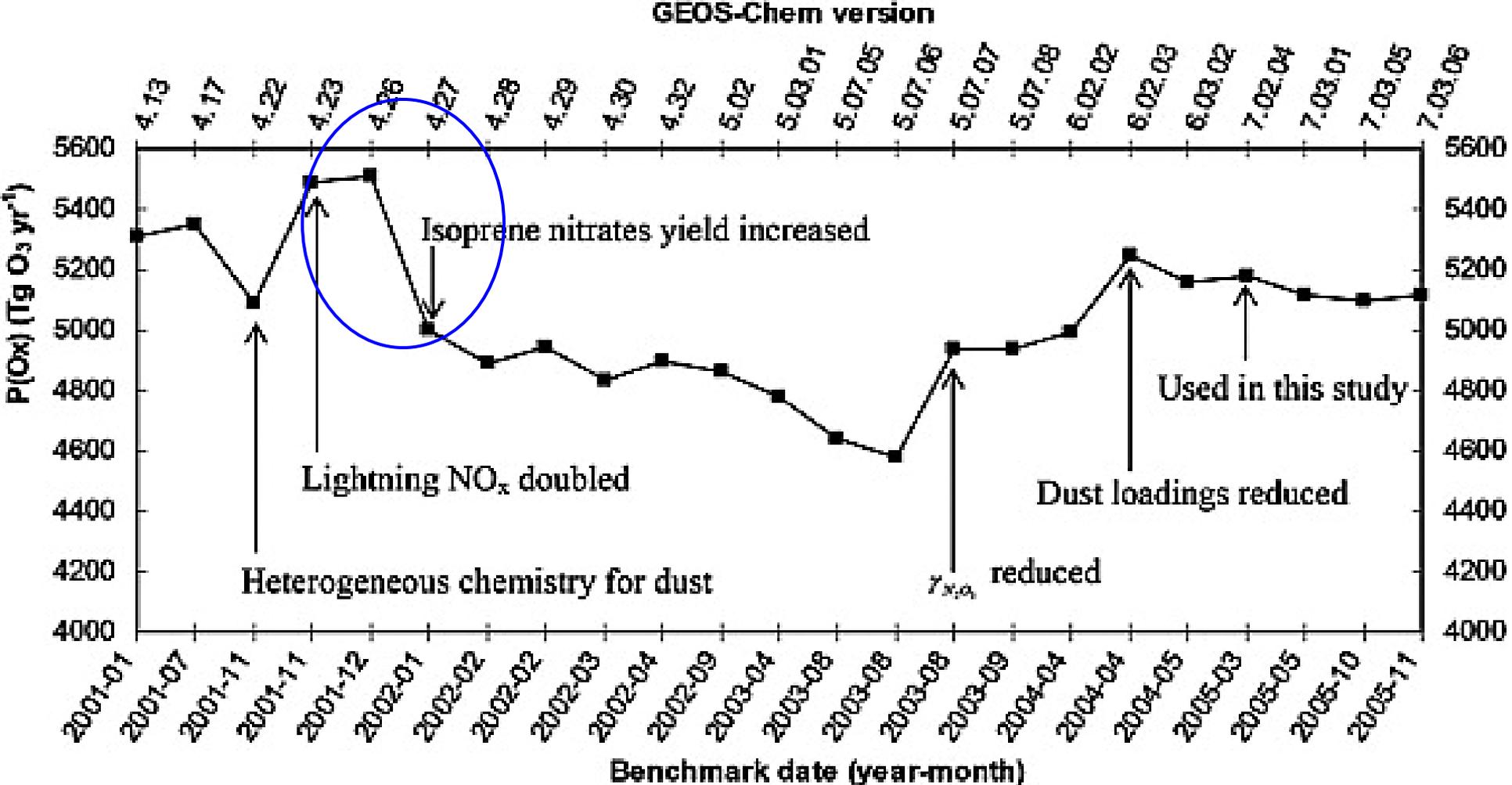
Do we understand NO_x/NO_y chemistry?

Isoprene and aromatics are important puzzles to examine

RONO₂

RONO₂ significant, often ignored





Wu et al, 2007

A ~10% change in global O₃ when isoprene branching ratio was changed from 4.4% to 12%.

- RONO_2 formation (especially from isoprene and other biogenics) is one of the key uncertainties in current and future AQ.
- Models with high RONO_2 production remove NO_x faster than they increase O_3 when isoprene emissions grow.
- RONO_2 are observed to be 15-25% of the NO_x sink. What happens to that N upon oxidation of the initial RONO_2 ?

The spectrum of models make every imaginable choice.

Measurements



Assumptions/Ideas that guide site our experimental strategy

1. VOC reactivity, NO_x chain termination rates, and T are the key parameters.
2. Local measurements of key species, their reaction products and precursors contain information about emissions and chemistry.
3. Biogenic VOC cannot be controlled—thus a crucial design parameter for control strategies is the fraction of VOC reactivity that we can control.
4. The same processes occur everyday at rates that depend on temperature, RH and available sunlight—thus day-to-day variability is one of the most important tests of our understanding.
5. NO_x reductions on weekends are one of the only “controlled” experiments we have available.

Strategy--SJV

Measure biogenic and anthropogenic organic molecules, including their reaction products.

Measure NO_x and its reaction products.

Measure HO_x and related reaction products

Examine as many closure relationships as possible to establish that detailed mechanisms of emissions, ozone and aerosol formation are correct.

Observe for long enough to capture statistics of day of week effects

Use these detailed evaluations to estimate how reality is different from predictions using a current generation AQ model.

The current SJV team

Allen Goldstein: VOC, CO, O₃, meteorological state variables

Ronald Cohen: NO, NO₂, Σperoxynitrates, ΣRONO₂, HNO₃

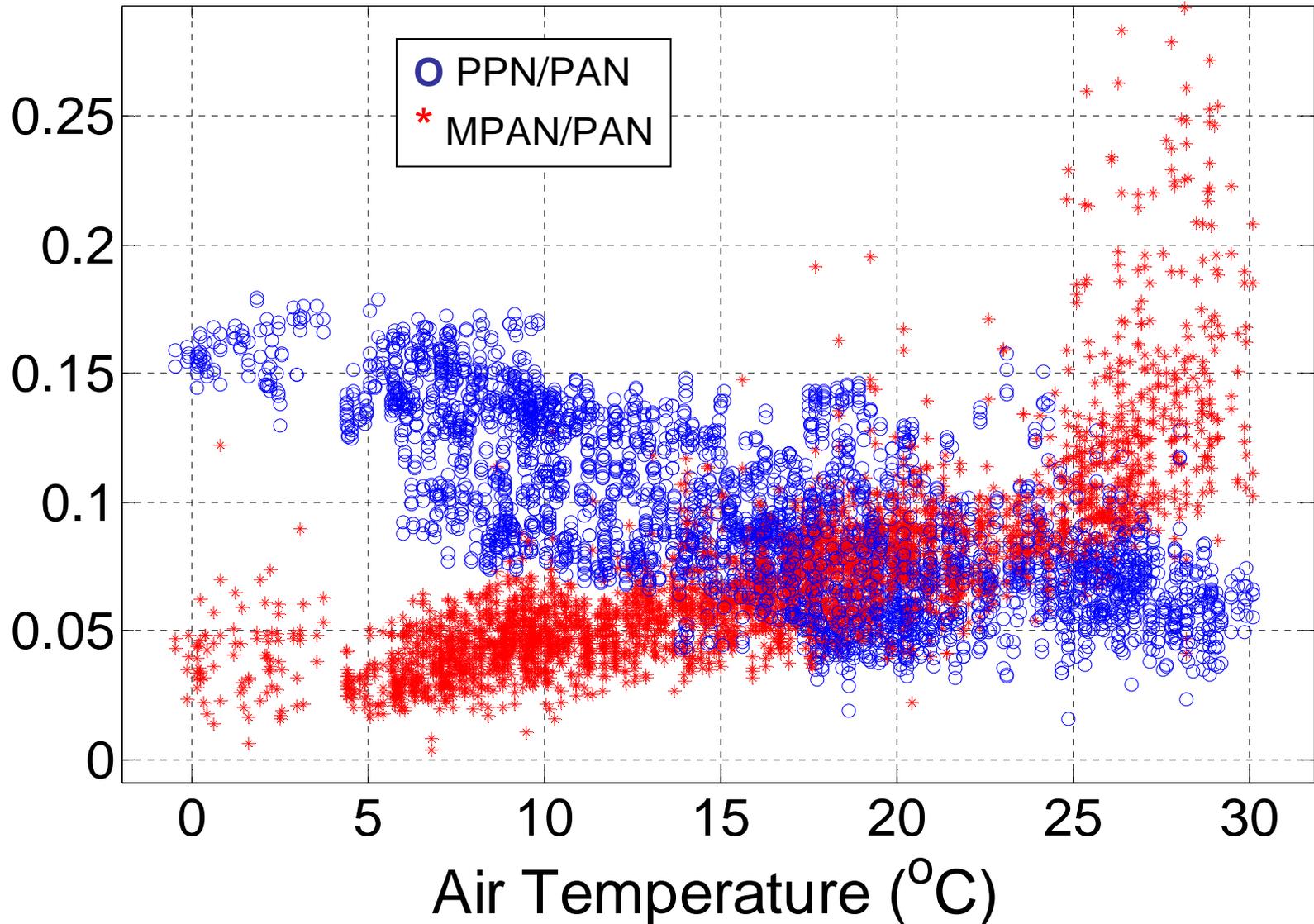
William H. Brune: OH, HO₂ ΣOH reactivity, potential aerosol mass

Joel Thornton: PAN, PPN, MPAN, RO₂NO₂ ...

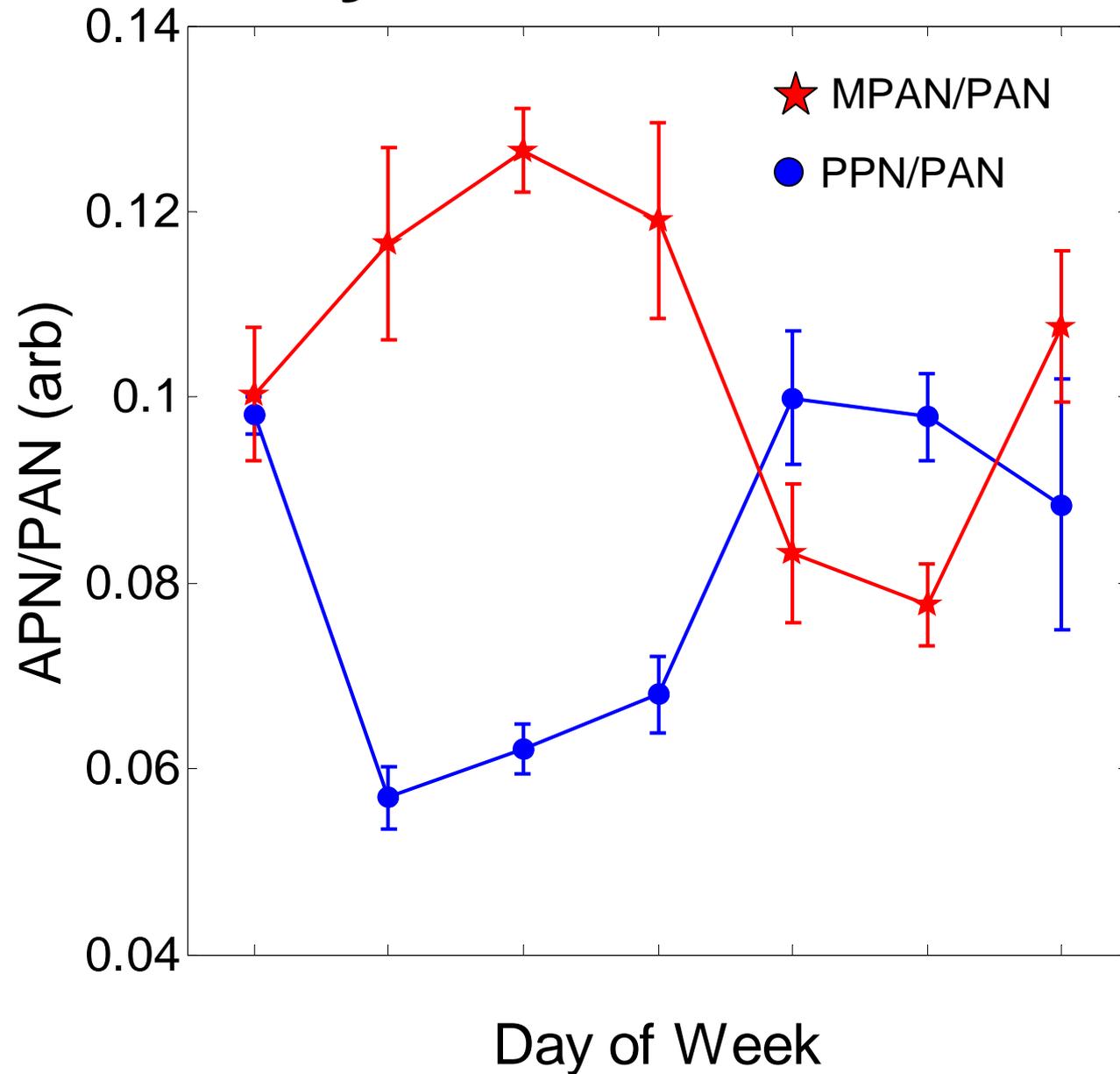
Frank Keutsch: H₂CO, HCOHCO, Σα-dicarbonyls

Paul Wennberg: HOOH, CH₃OOH, HNO₃, HO₂NO₂, HCN, other peroxides and several non-traditional isoprene oxidation products

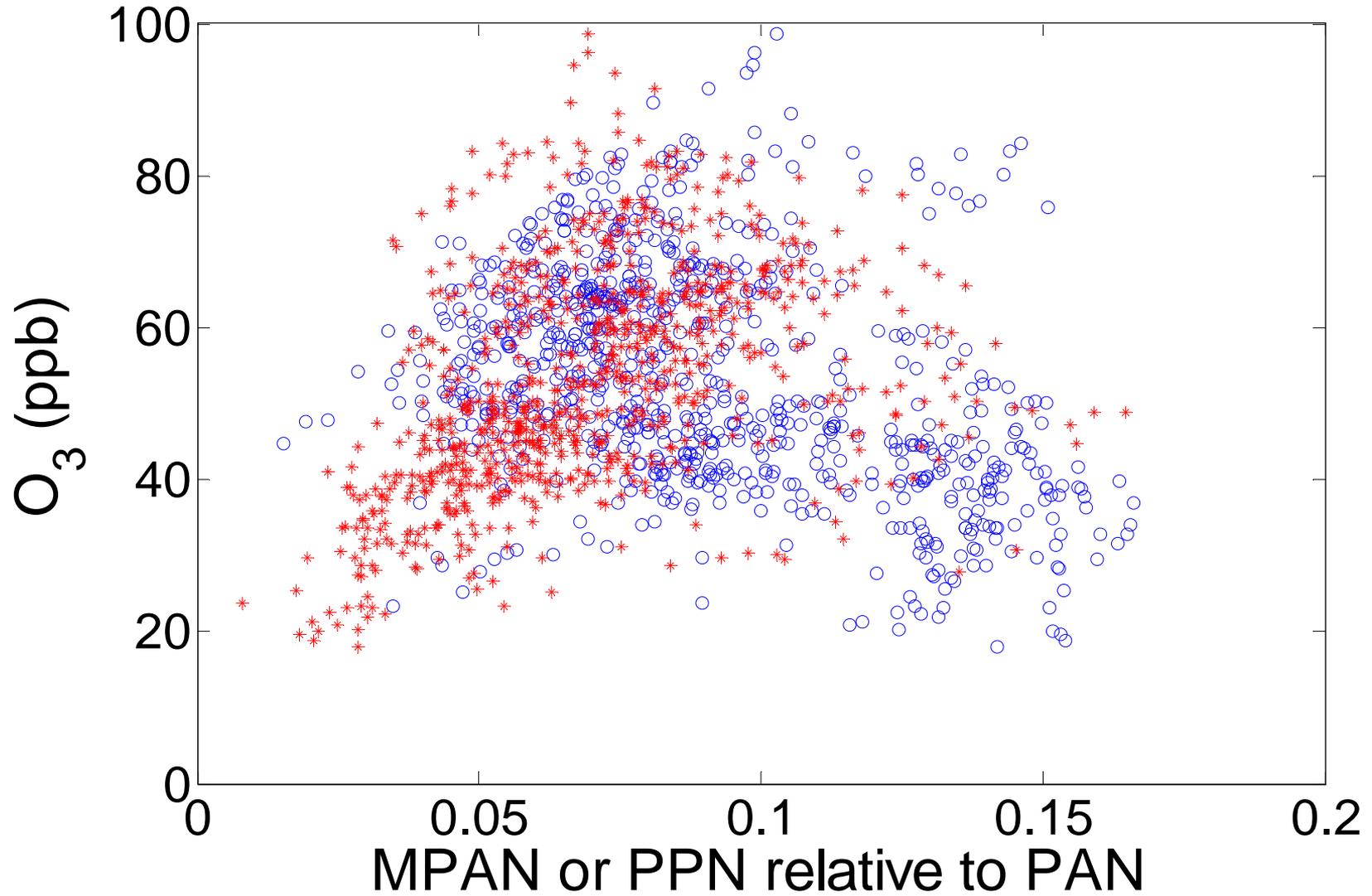
MPAN/PAN and PPN/PAN vs. T



Day of Week Effect

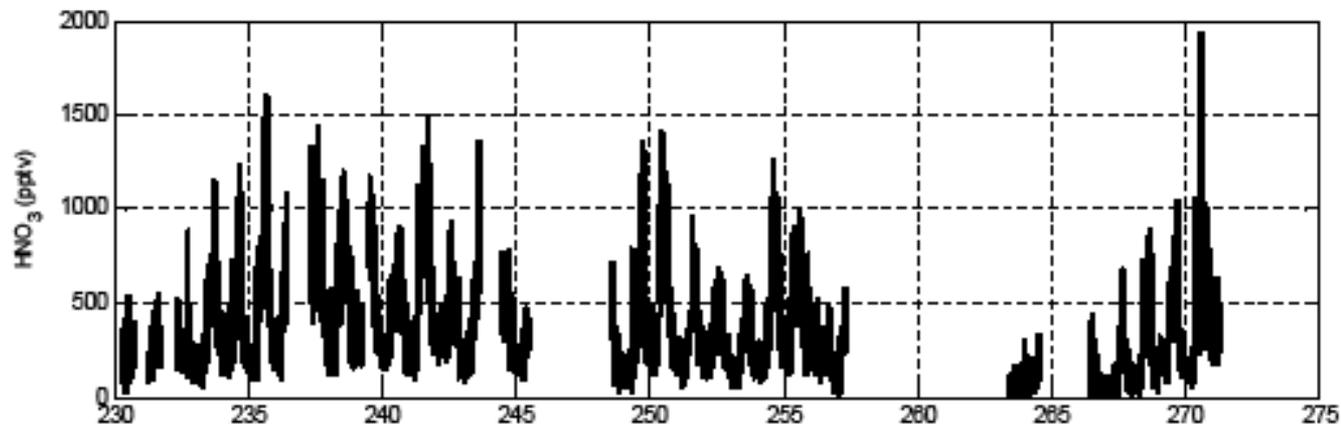


Ozone vs. MPAN/PAN and PPN/PAN

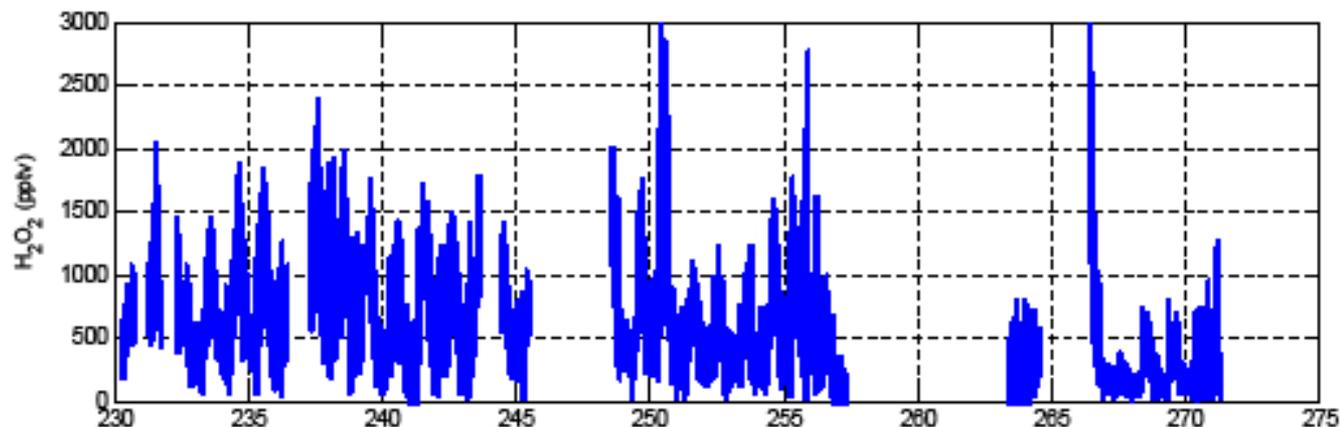


Caltech

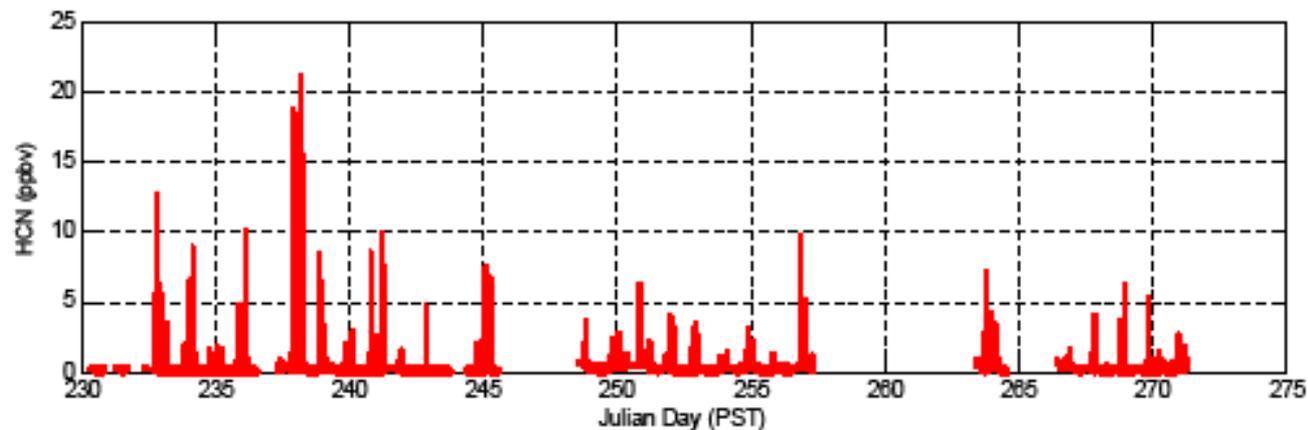
HNO_3



H_2O_2

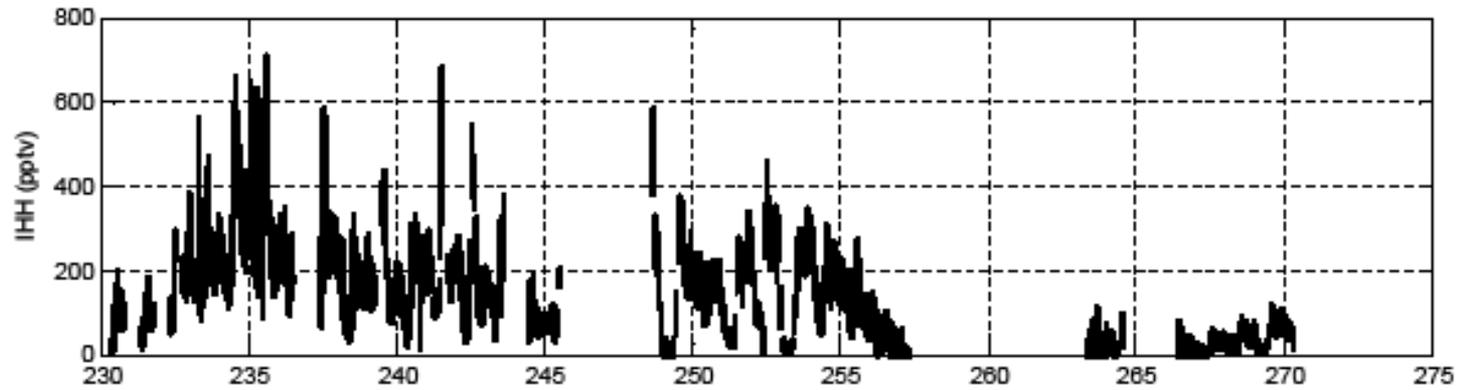


HCN

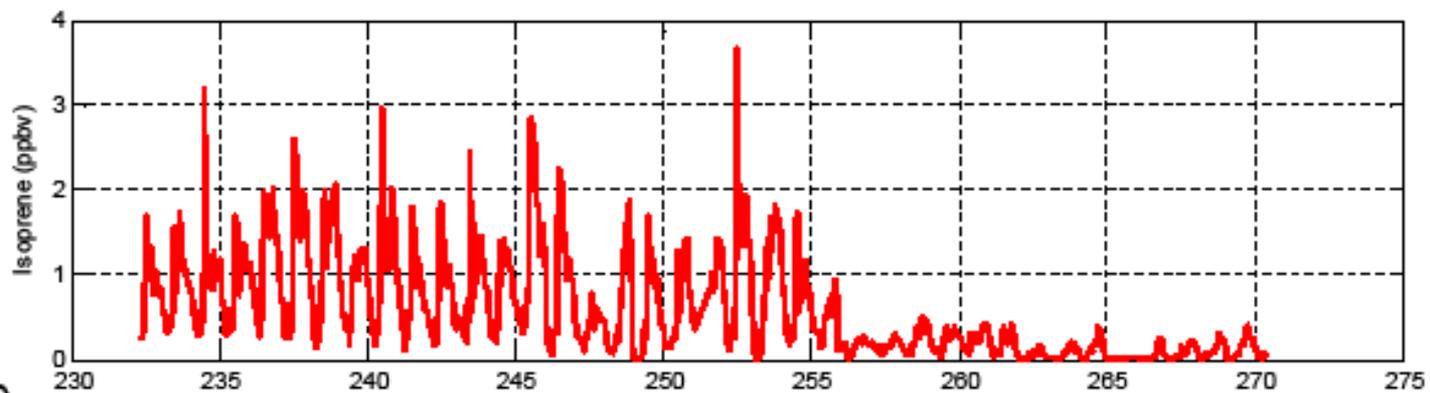


Caltech

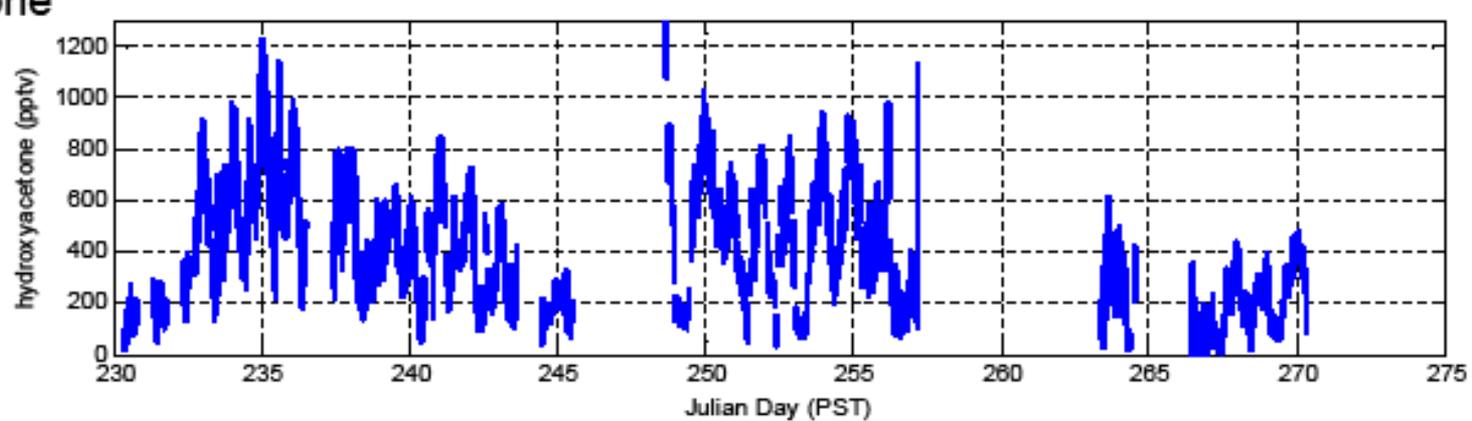
Isoprene HH



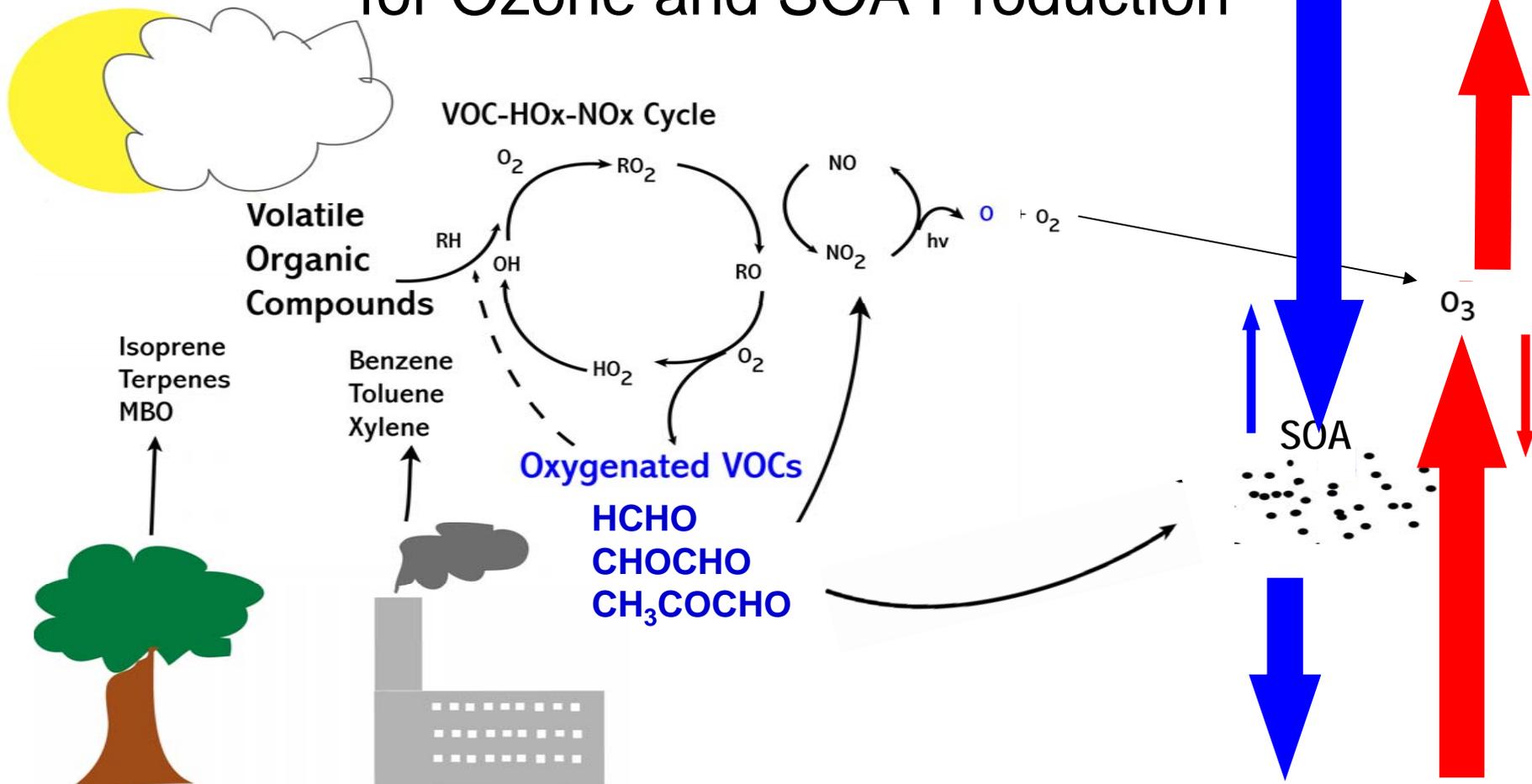
Isoprene



Hydroxyacetone



α -dicarbonyls and Formaldehyde: Central OVOOCs for Ozone and SOA Production



- Formaldehyde proven tracer of VOC oxidation chemistry
- α -dicarbonyls are higher generation oxidation products of biogenic VOCs ¹, thus allow new insights into VOC oxidation chemistry
- Glyoxal contributes to SOA (>15% of SOA proposed for Mexico City ²)

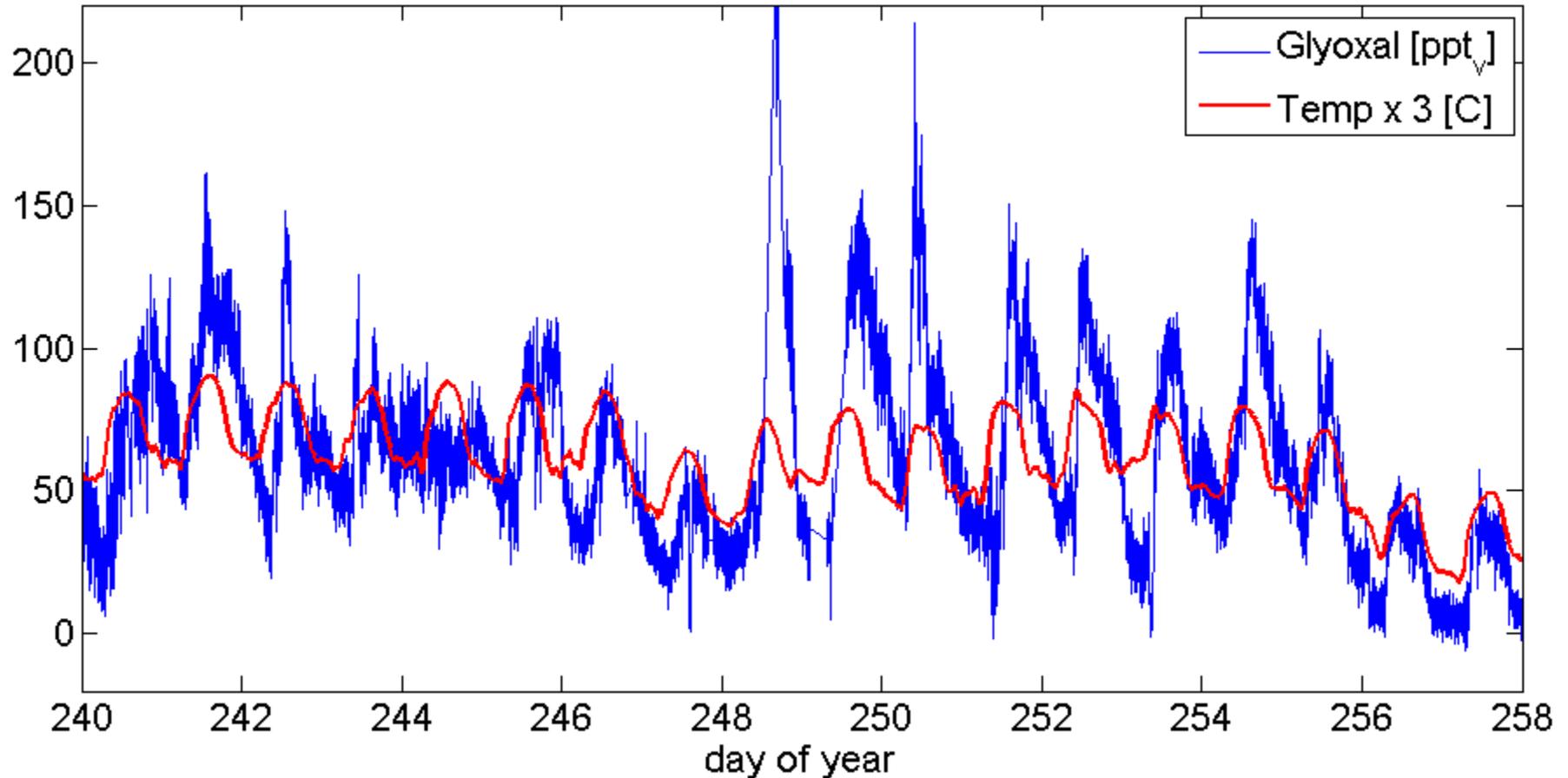
¹ Master Chemical Mechanism; ² Volkamer, R., et al., Geophys. Res. Lett. 34, L19807, (2007)

The Madison Laser-Induced Phosphorescence Instrument: Direct, Highly Specific and Sensitive Measurement of α -dicarbonyls

- Precision (1σ) 2 ppt_v/min in the field (more than order of magnitude better than other instrumentation)
- Highly specific (no inlet effects detected, no interference from NO_x, O₃, H₂O, VOCs or OVOCs)
- First LIP instrument for atmospheric measurements
- Custom Ti:Sapphire laser (440-441 nm; $\Delta\nu=0.04$ cm⁻¹; 80 mW)
- Tuning fast (25 ms) and piezo controlled
- Wavemeter for wavelength tracking
- White Cell multipass configuration
- Digital gating and photon counting PMT

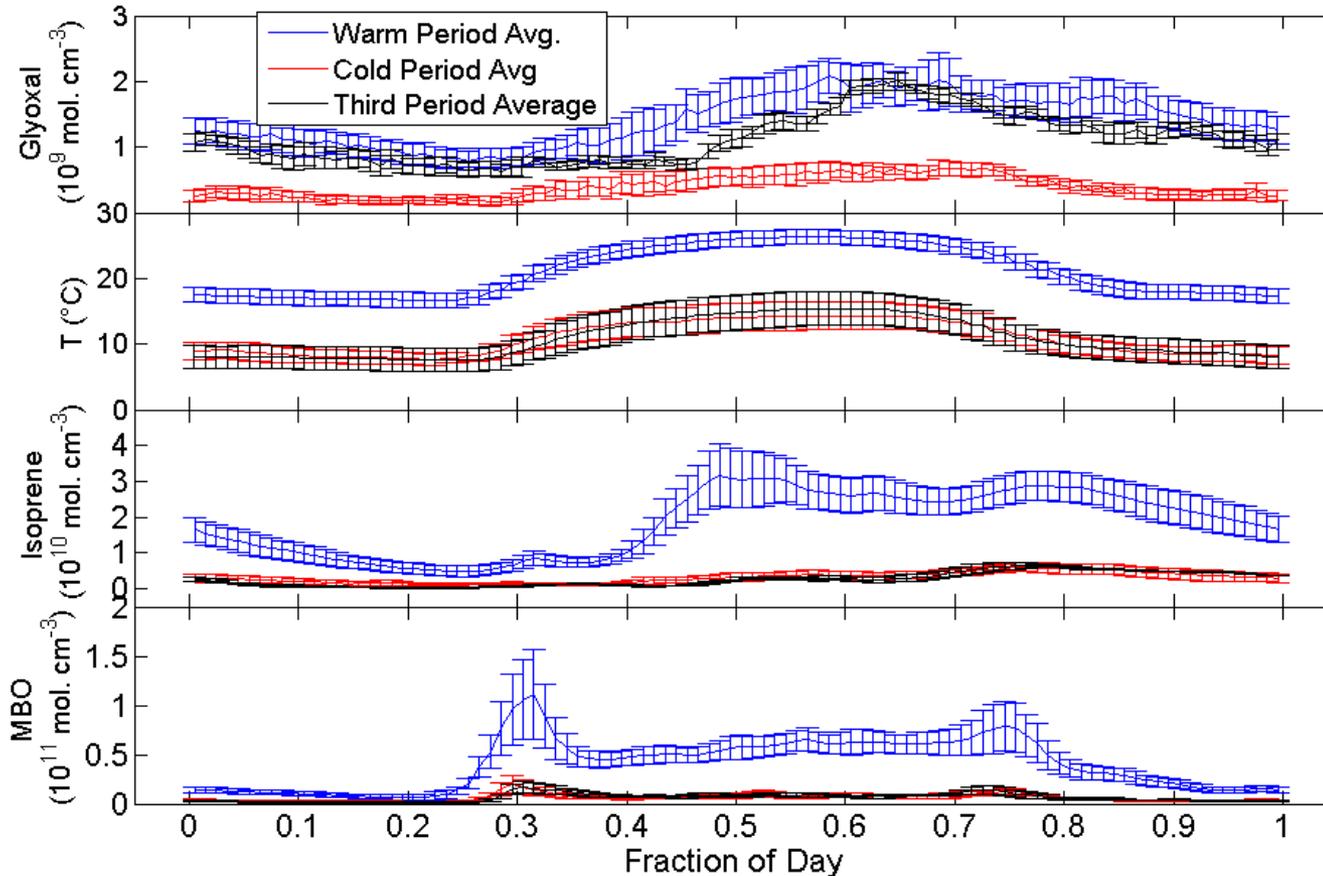


Analysis of VOC Oxidation: Biogenic vs. Anthropogenic Precursors of Glyoxal from BEARPEX 2007



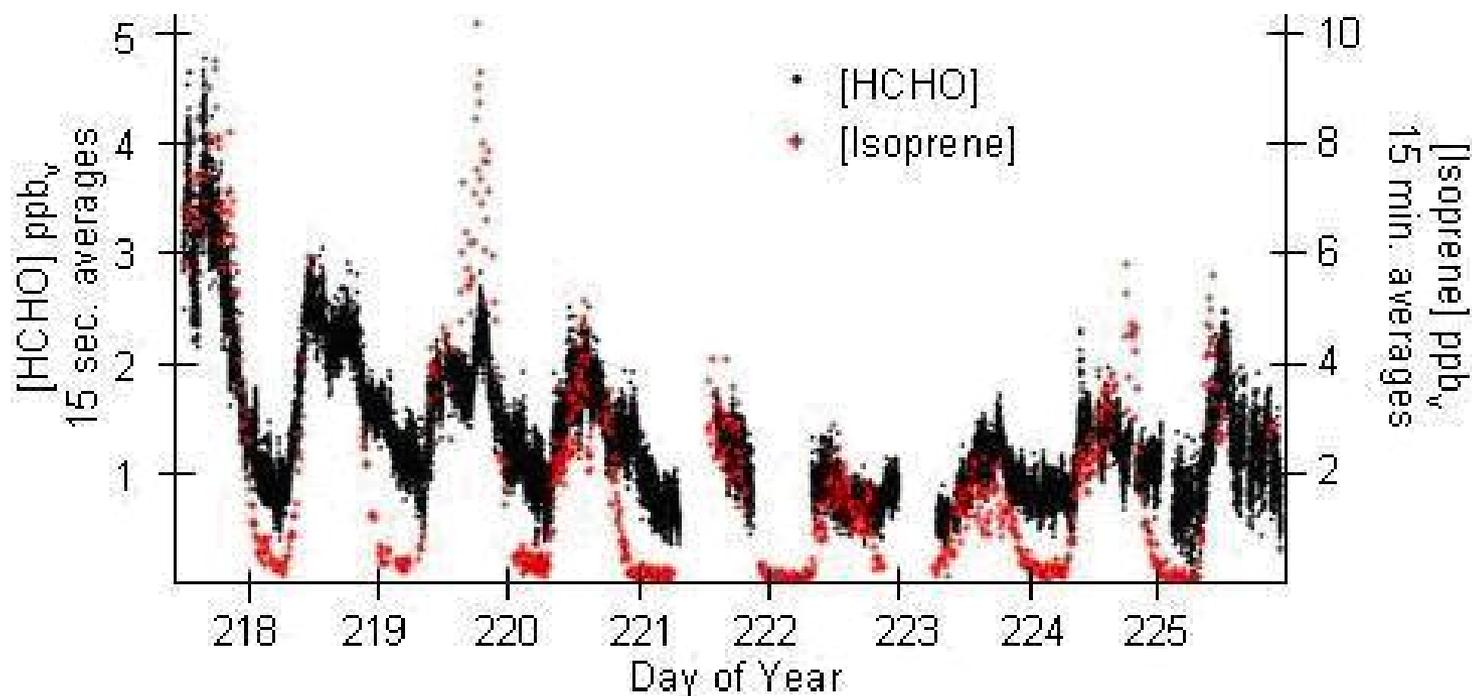
- High glyoxal mixing ratios observed
- Overall good correlation with isoprene and MBO
- Days 268-271 show higher glyoxal/[isoprene,MBO]

Analysis of VOC Oxidation: Biogenic vs. Anthropogenic Precursors of Glyoxal from BEARPEX 2007

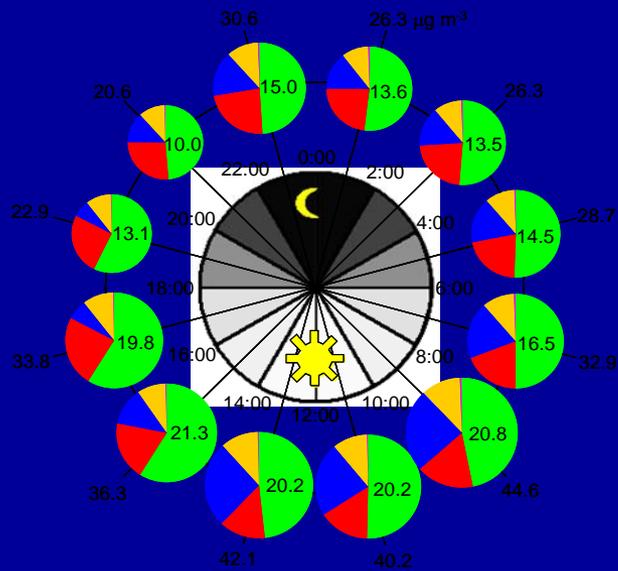


- Change of biogenic and anthropogenic precursors for different T-regimes show that biogenics are main glyoxal precursor
- During third period glyoxal precursors are under investigation

Formaldehyde Measurements PROPHET 2008



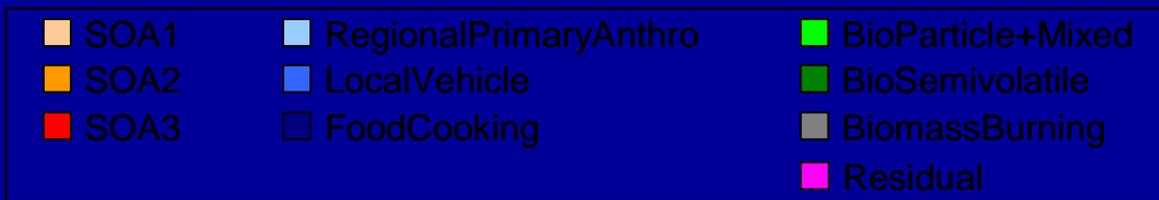
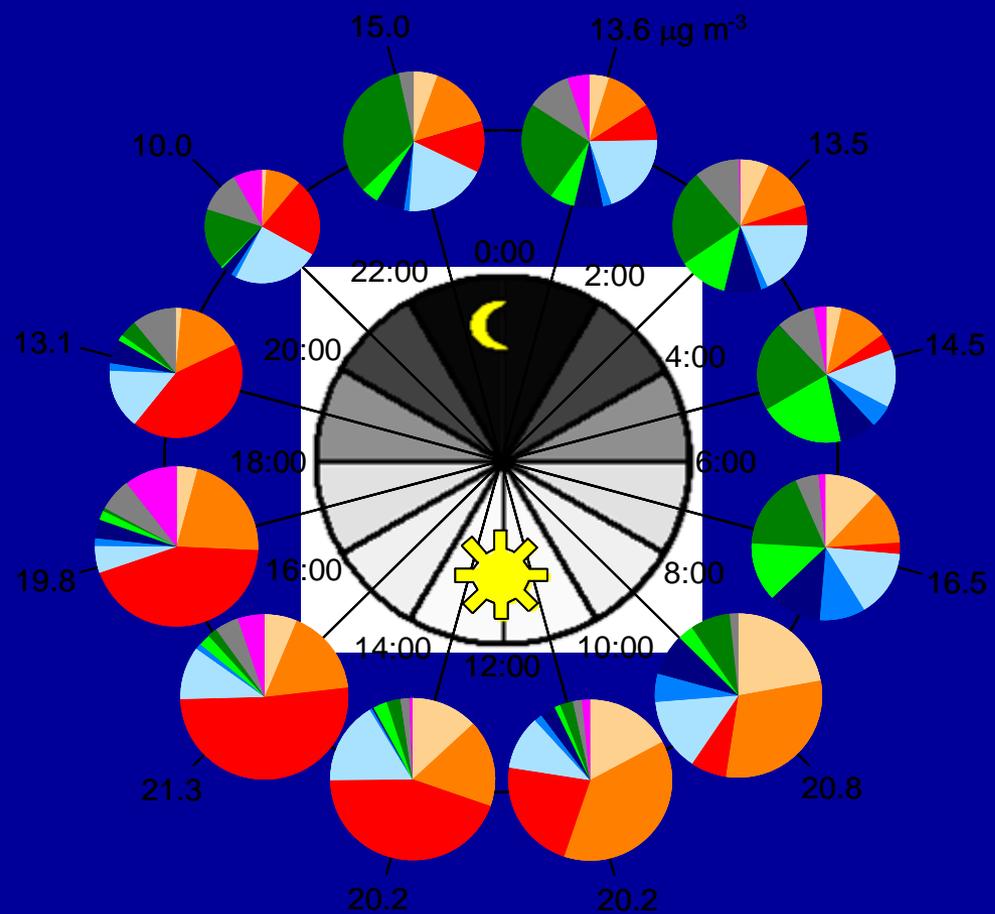
- Field test of the formaldehyde LIF instrument was successful
- Prototype laser tested in Madison with ambient measurement
- The upgraded instrument will allow fast highly sensitive measurements including the first formaldehyde flux measurements via eddy correlation



AMS Total Organic Aerosol = 10.0 - 20.8 $\mu\text{g m}^{-3}$

Riverside Summer

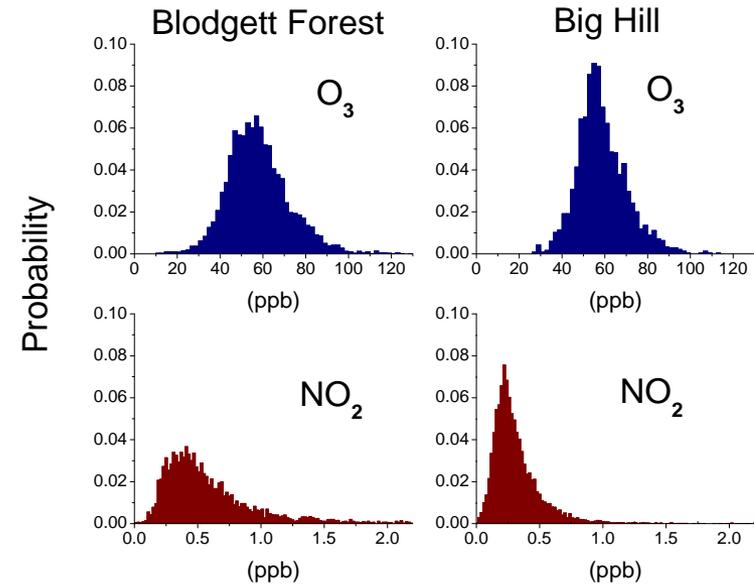
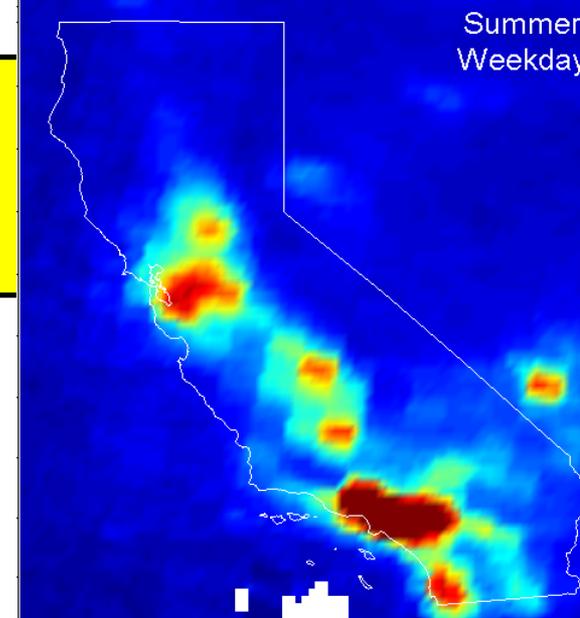
TAG-defined Organic Aerosol Sources

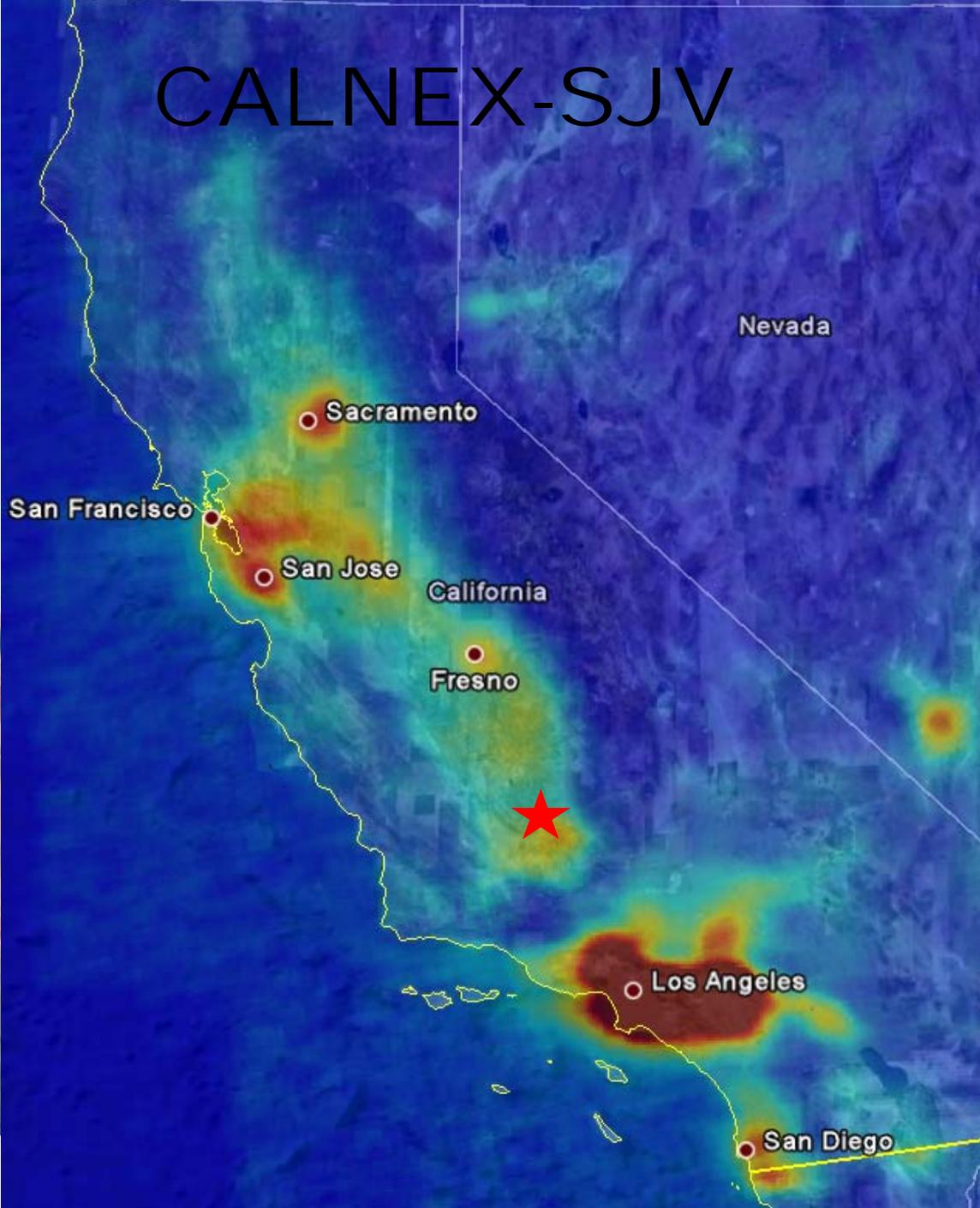
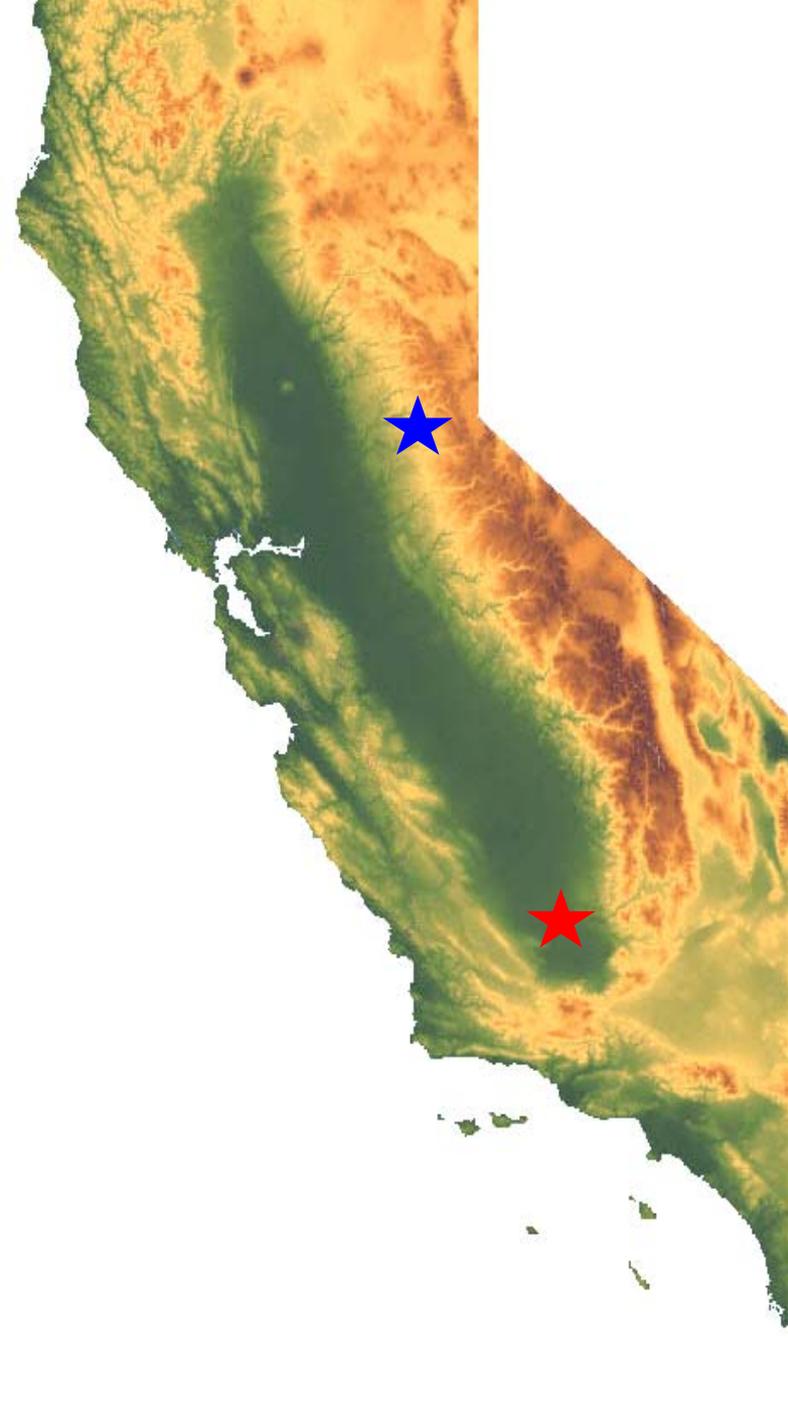


AMS Total Organic Aerosol = 10.0 - 20.8 $\mu\text{g m}^{-3}$

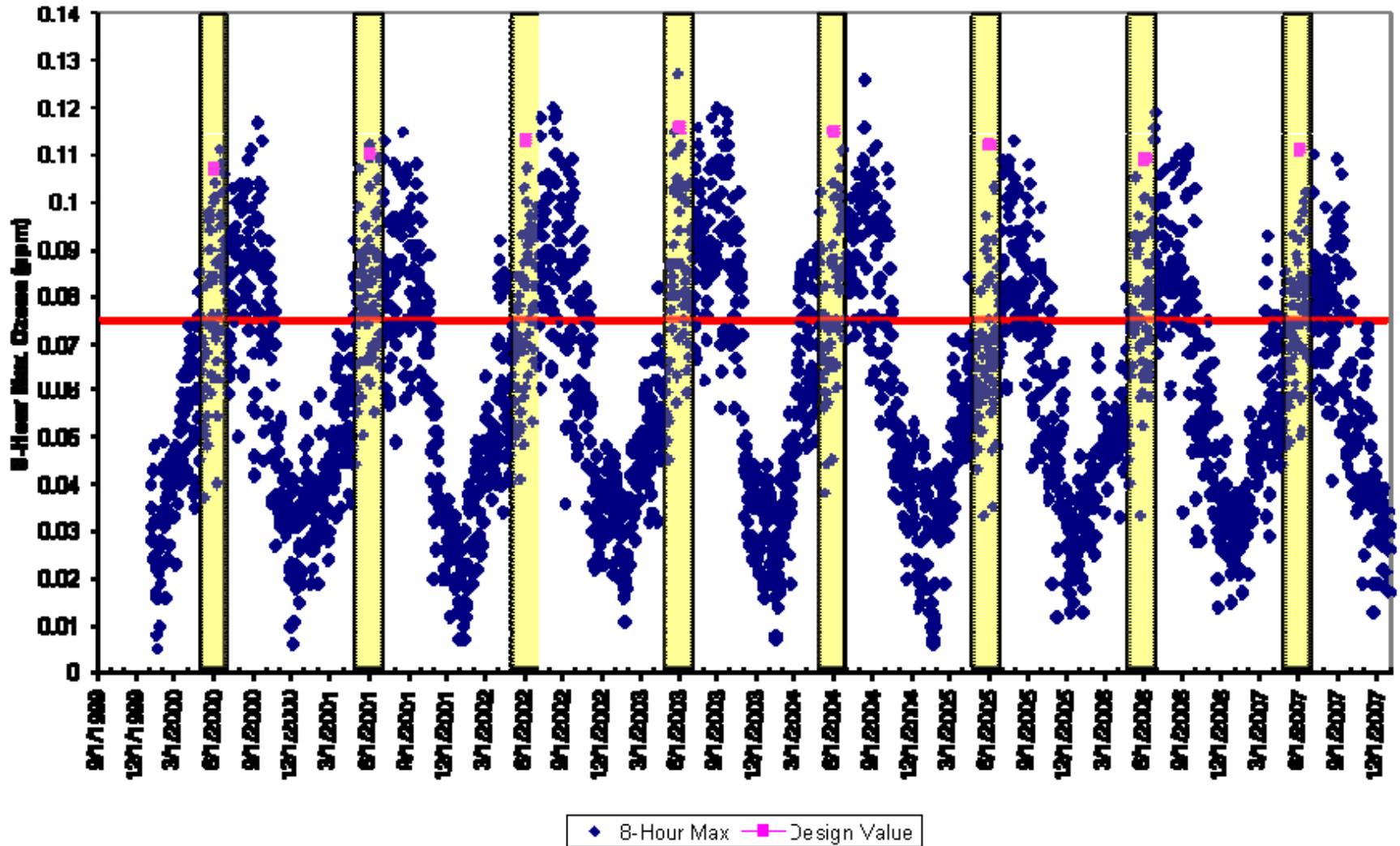
2010 Vision for AQ

- In 2010 satellites will be major contributors to our understanding of AQ, with daily coverage for PM, NO₂, H₂CO and CO.
- In 2010 the comparatively low cost of modeling will lead to a new opportunity to use and emphasize one statistics within long term data sets.
- In 2010 the capabilities for detailed chemical tests of aerosol and O₃ (and other chemicals) models will bring our attention to establishing the precursors are right first, so we can show the end products we model are correct for the right reasons.





8-Hour Max. at Arvin



Strategy--Partners

Integrate our measurements with a wide range of partners during CalNex

Integrate with Satellite based observations of NO₂, aerosol and land-cover

Integrate our measurements with a broad perspective based on observations collected in previous CA experiments by the same teams.

BEARPEX, ARB-ARCTAS, INTEX-B, ITCT 2002

Work together to bring new resources and additional measurements to CALNEX overall and to this site.

Thank you

The image features a solid blue background. In the top-left corner, the text "Thank you" is written in a yellow, sans-serif font. In the bottom-right corner, there are several decorative, wavy, light-blue lines that create a sense of movement and depth.