Nitrogen Oxide Emissions and Chemistry: Implications for Air Quality Control Strategies in a Warmer Climate

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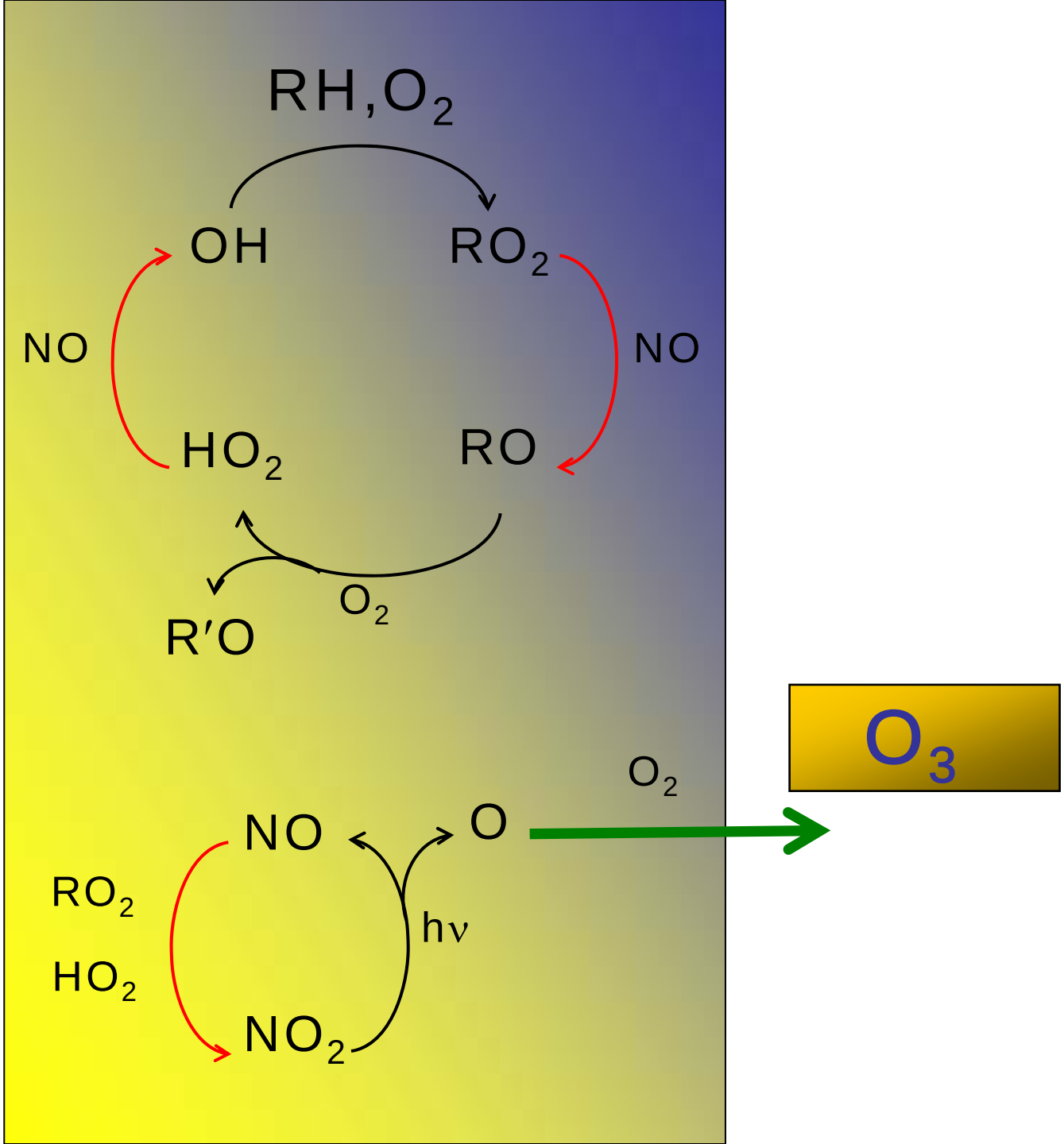
Chemistry

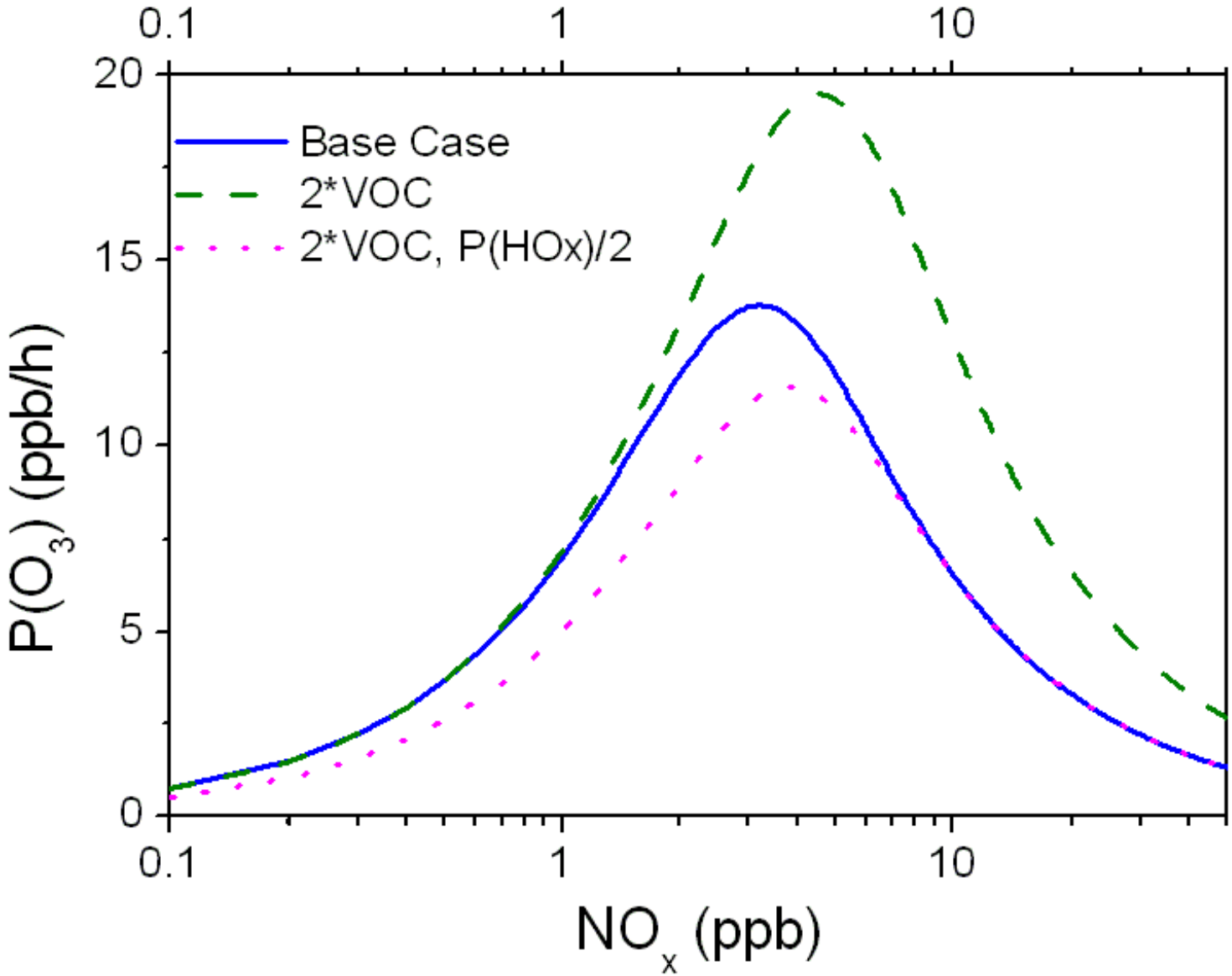
Catalytic Cycles

HO_x Cycle

NO_x Cycle



Photochemical Ozone Production
NO_x, VOC Reactivity, HO_x production



Chain Termination

HO_x- HO_x

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$$

$$HO_2 + RO_2 \longrightarrow ROOH + O_2 \quad ????$$

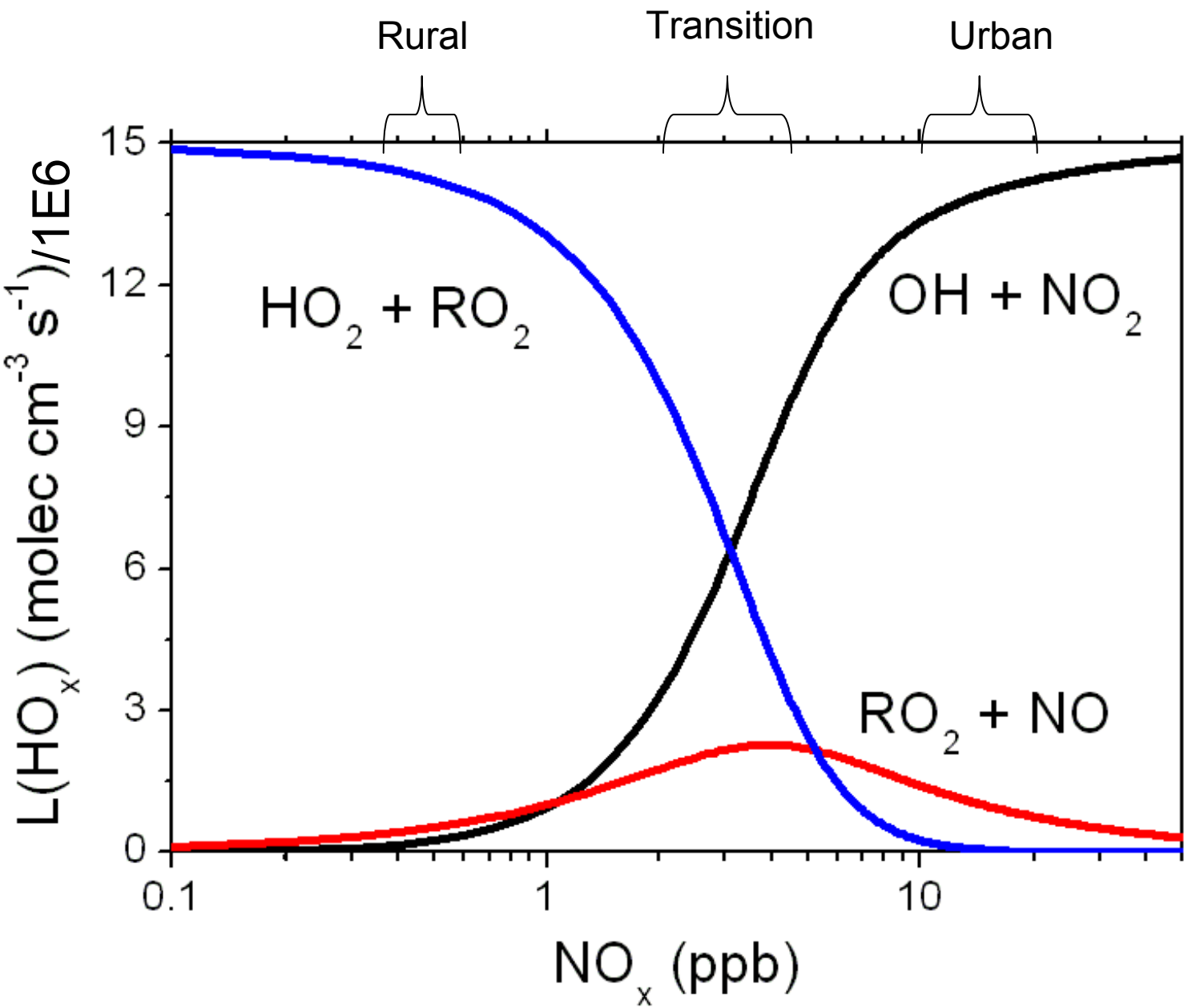
$$HO_2 + OH \longrightarrow H_2O + O_2$$

NO_x- HO_x

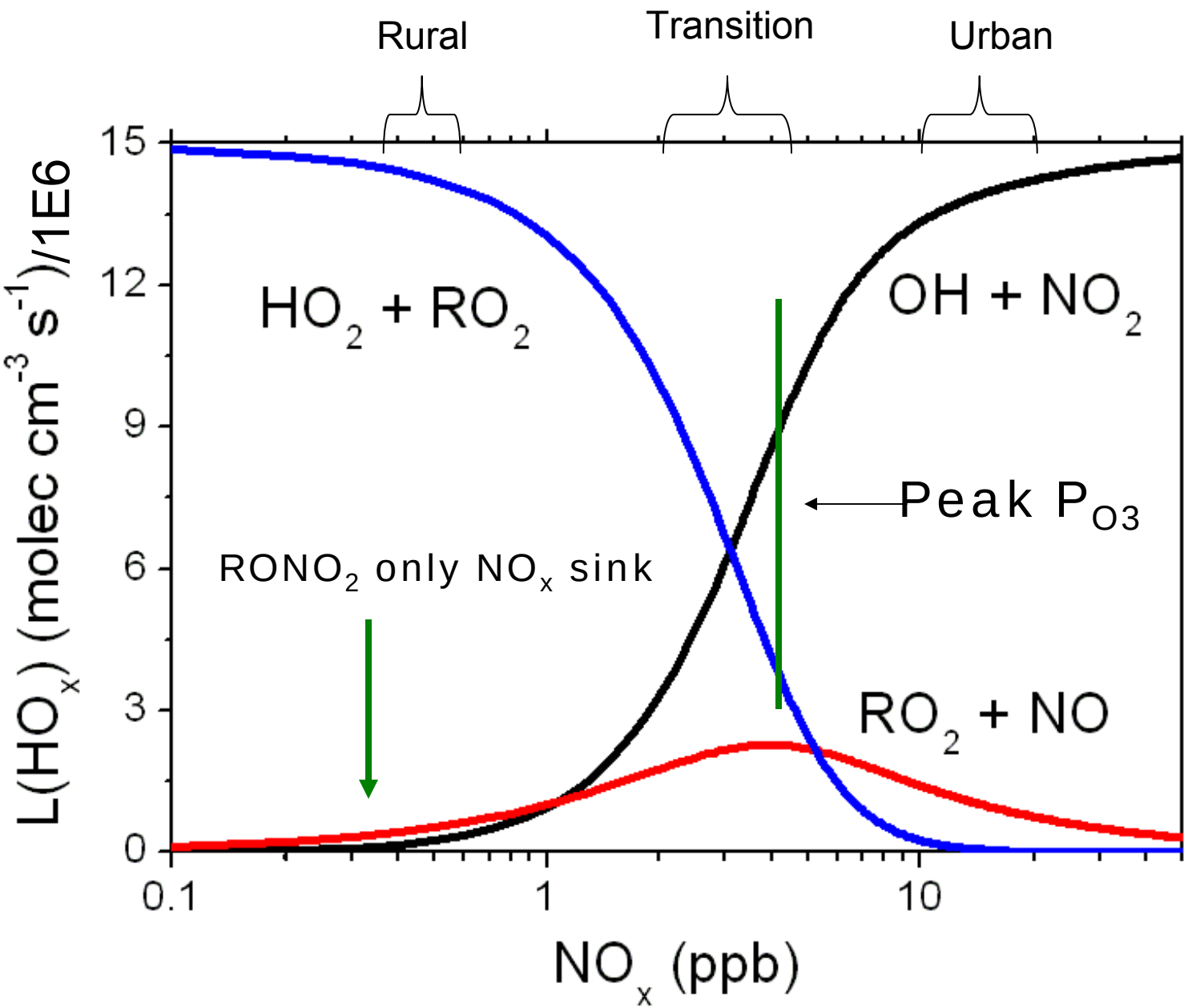
$$NO_2 + OH \xrightarrow{M} HNO_3$$

$$RO_2 + NO \xrightarrow{M} RONO_2 \quad ????$$

NO_x and HO_x Radical Termination



NO_x and HO_x Radical Termination



Warmer climate

- Most reactions faster
- More H_2O (same RH)
- More evaporative emissions
- More biogenics

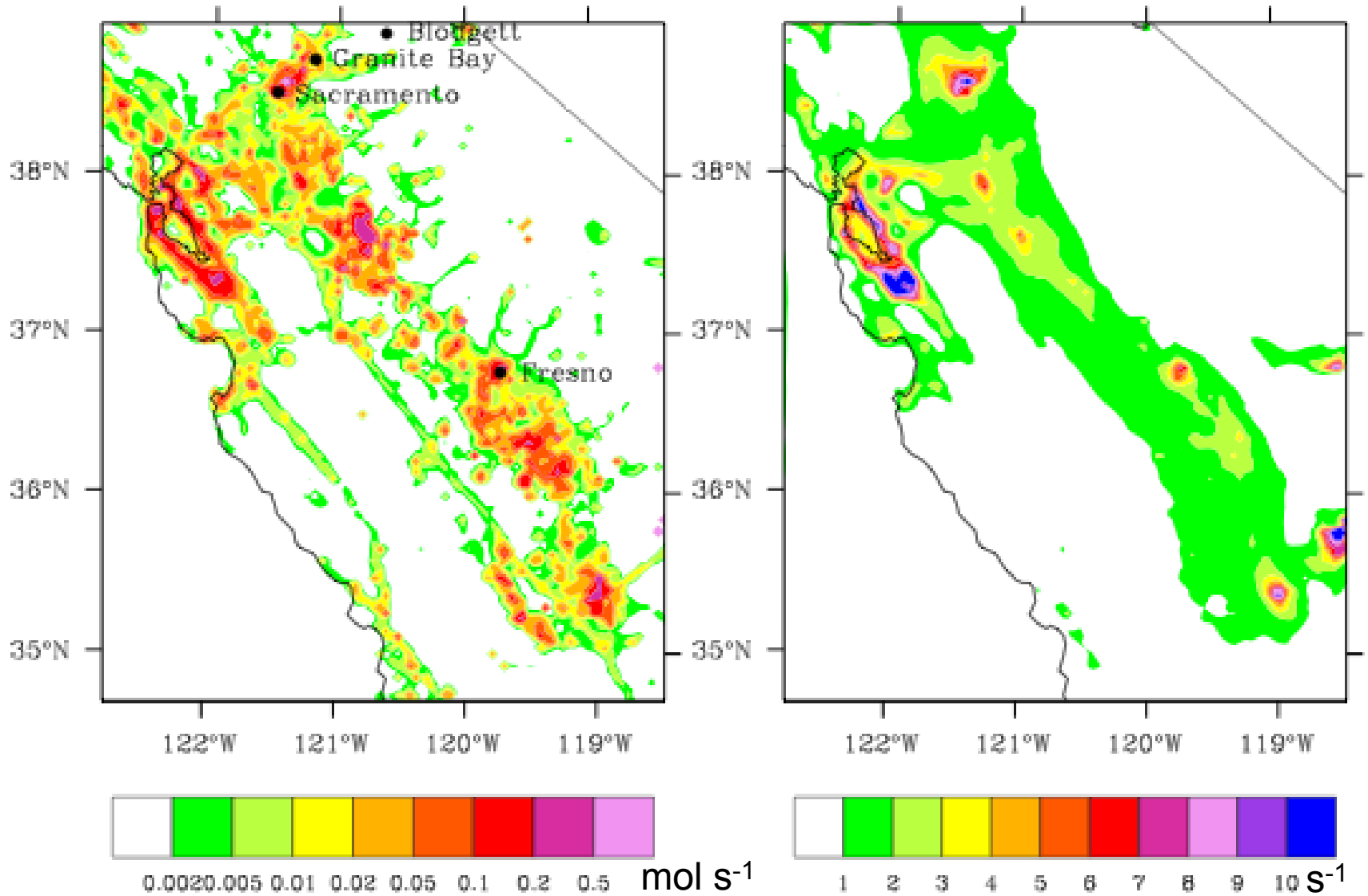
Future

- Controls expected to produce dramatic local NO_x reductions in CA but controls insufficient to prevent global increases in NO_x and O_3

VOC Reactivity

Steiner et al 2007

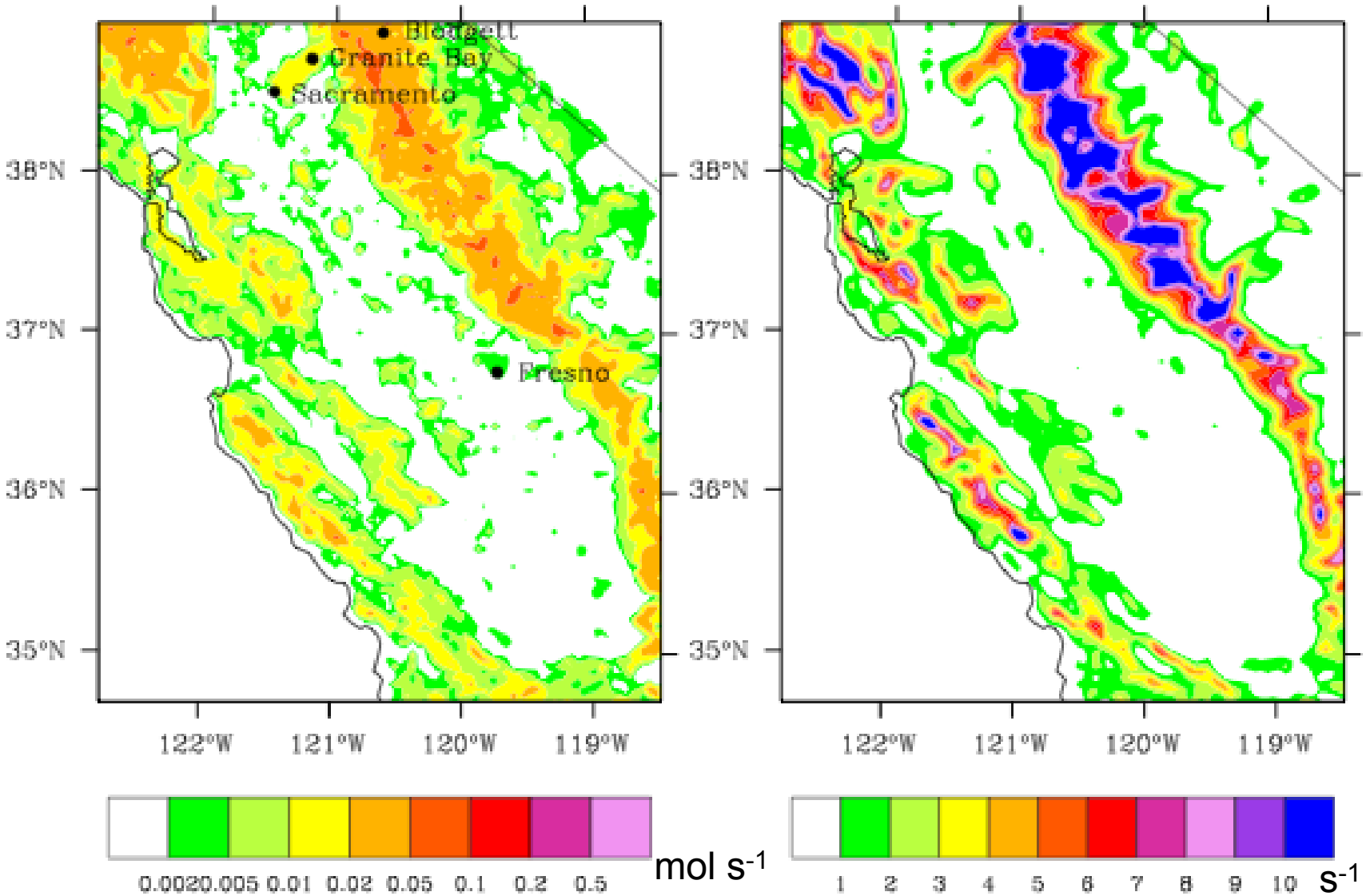
Anthropogenic VOC: Emissions and R_{VOC}



VOC Reactivity

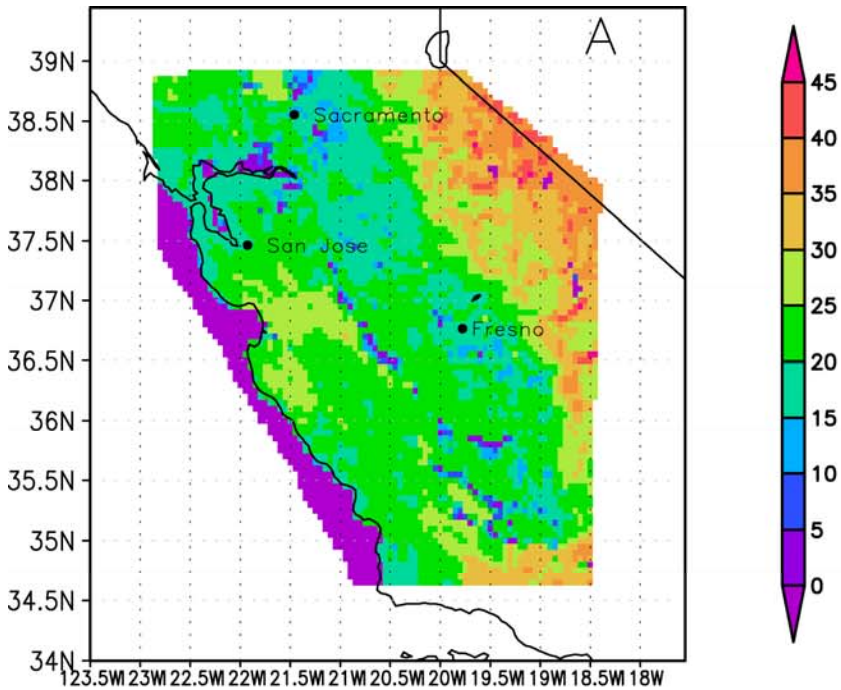
Steiner et al 2007

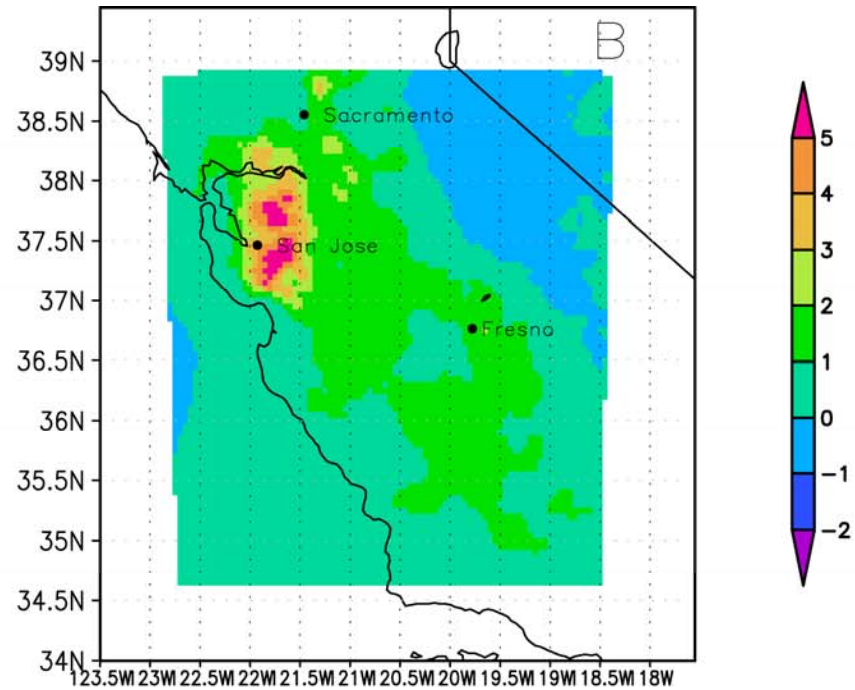
Biogenic VOC: Emissions and R_{VOC}



Effect of ΔBVOC on Ozone

% Increase in BVOC → Change in O_3 (ppb)



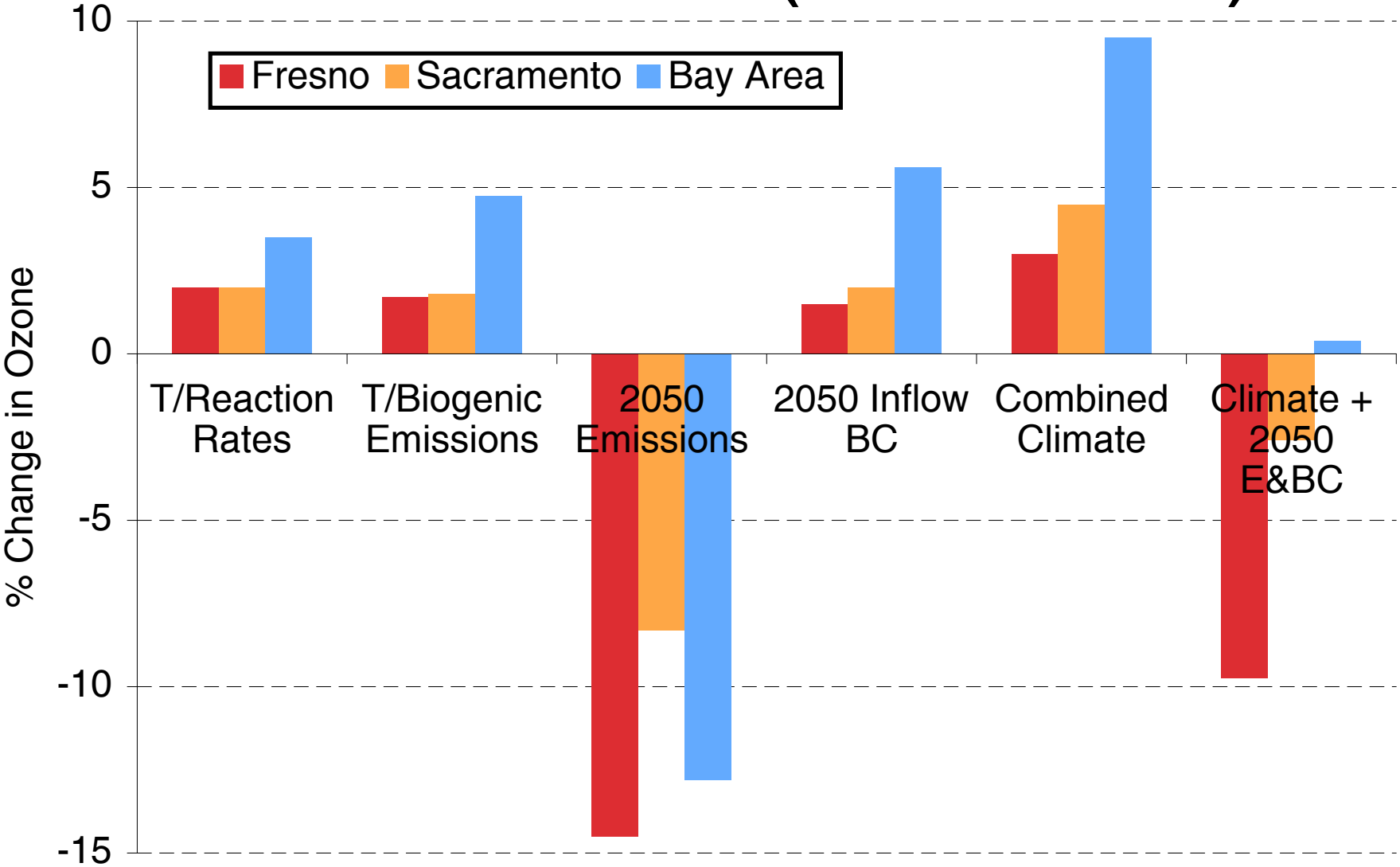


Biogenic emissions of isoprene & MBO peak at 37ºC

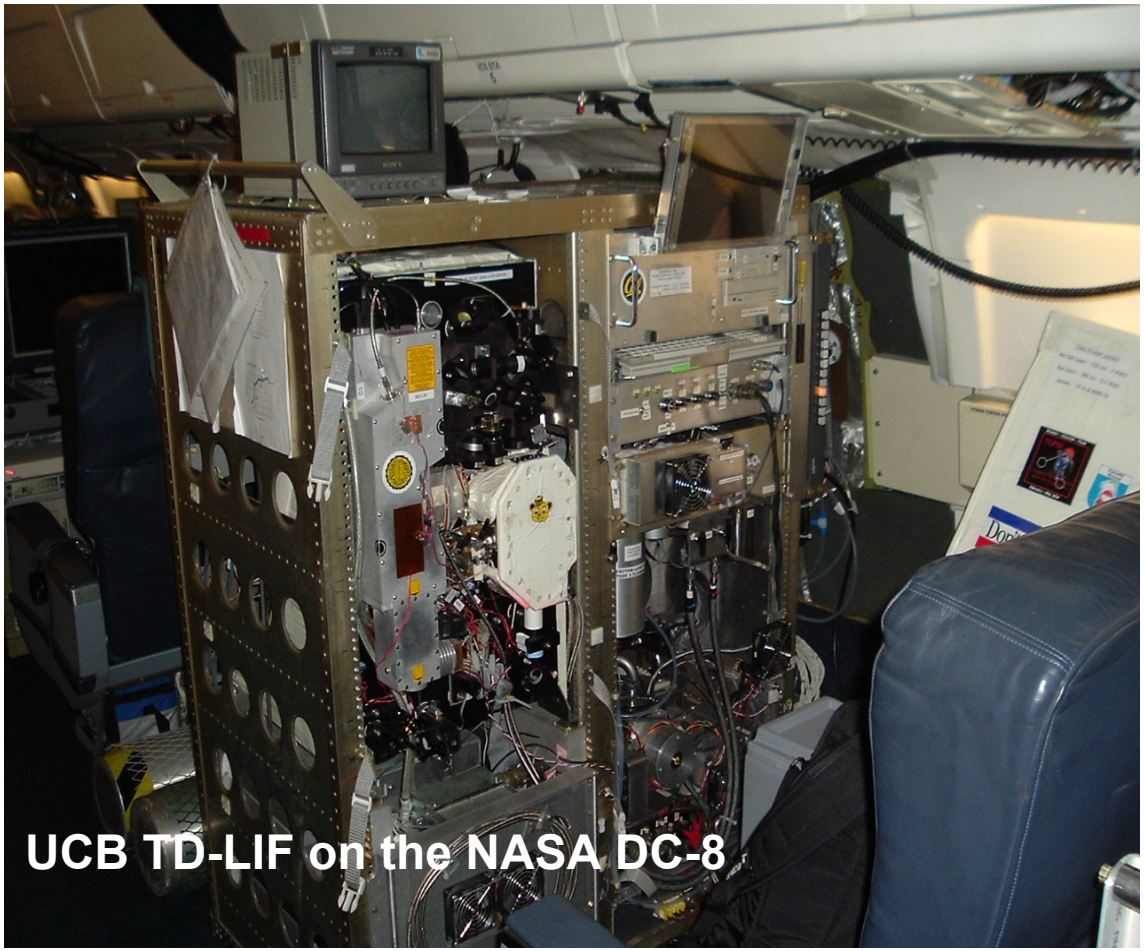
Terpene emissions increase exponentially with T

Steiner et al 2006

Steiner et al. (JGR 2006)



Berkeley LIF NO_2



- Direct and specific
- accurate: ±5%, 1σ
- sensitive: 1ppt/min, S/N=2
- detection limit <1ppt
- ~ 4 days unattended

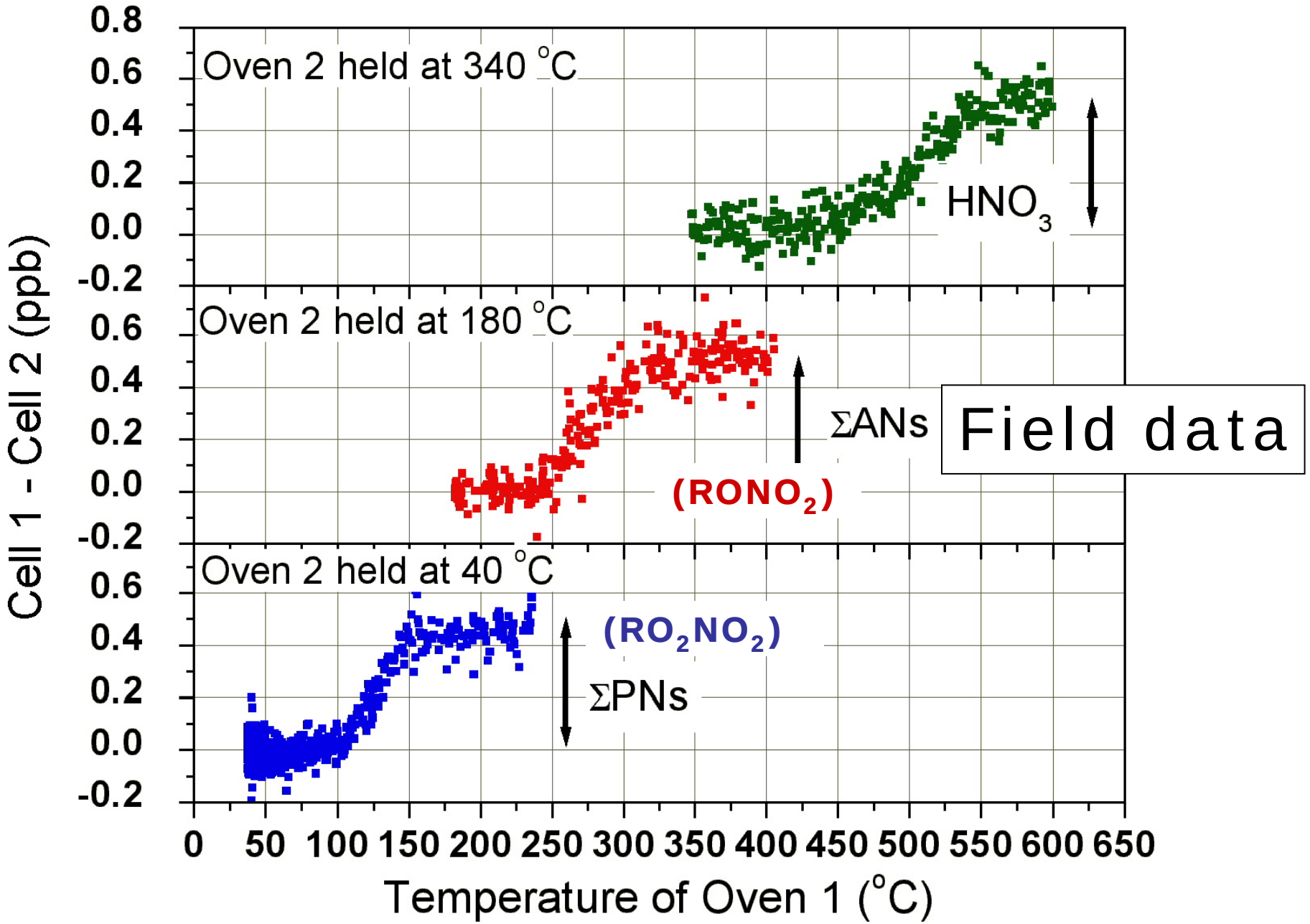
- Also, smaller, lower cost versions using blue (408nm) and red (638 nm) lasers 20ppt/min

Thornton, et al. Anal. Chem. **72**, 528 2000
Cleary, et al. Appl. Opt. **41**, 6950, 2002

ΣPNs, ΣANs, &
HNO_3 + heat $\rightarrow$
RO_x + NO_2

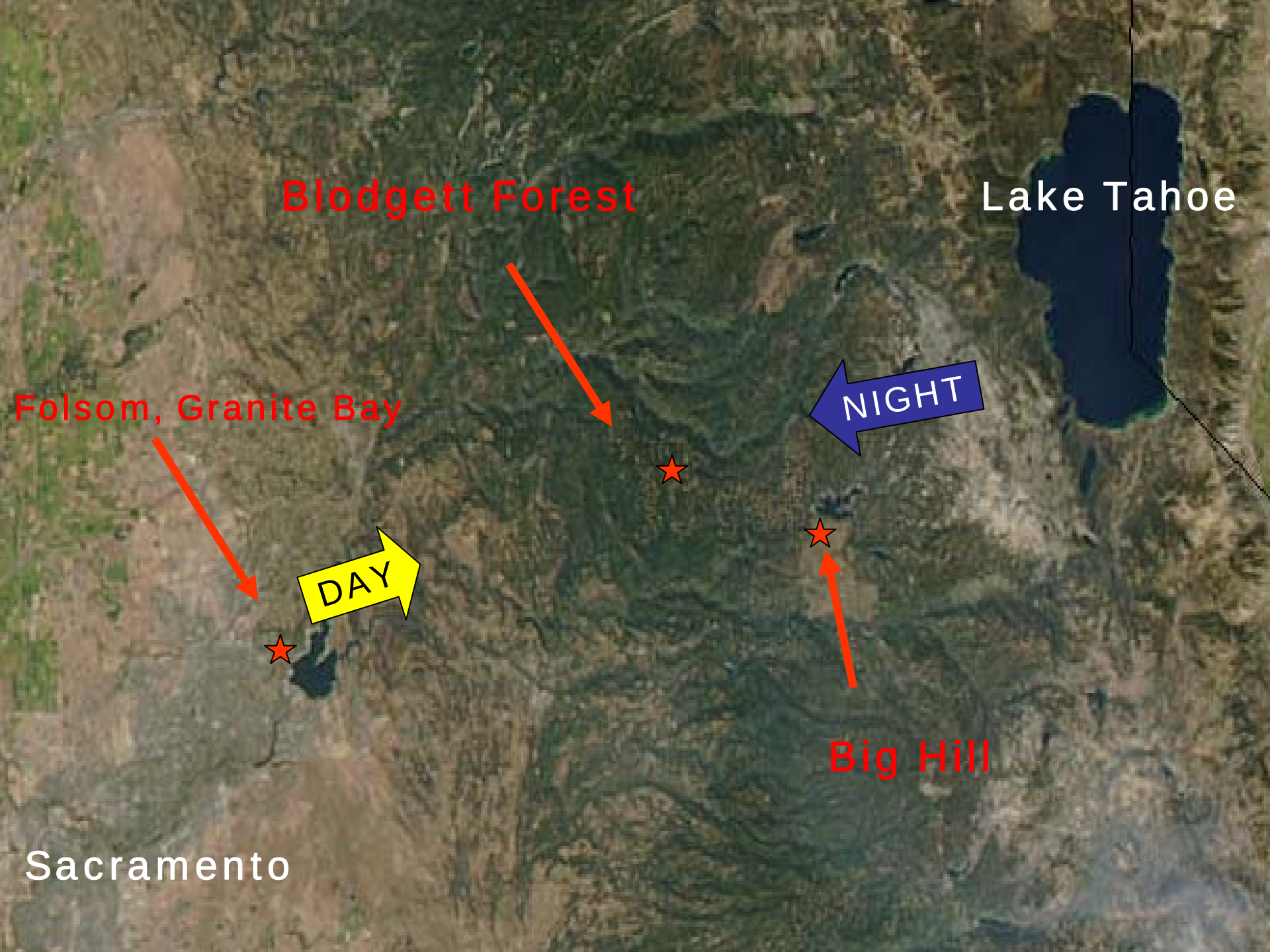
Thermal Dissociation-LIF

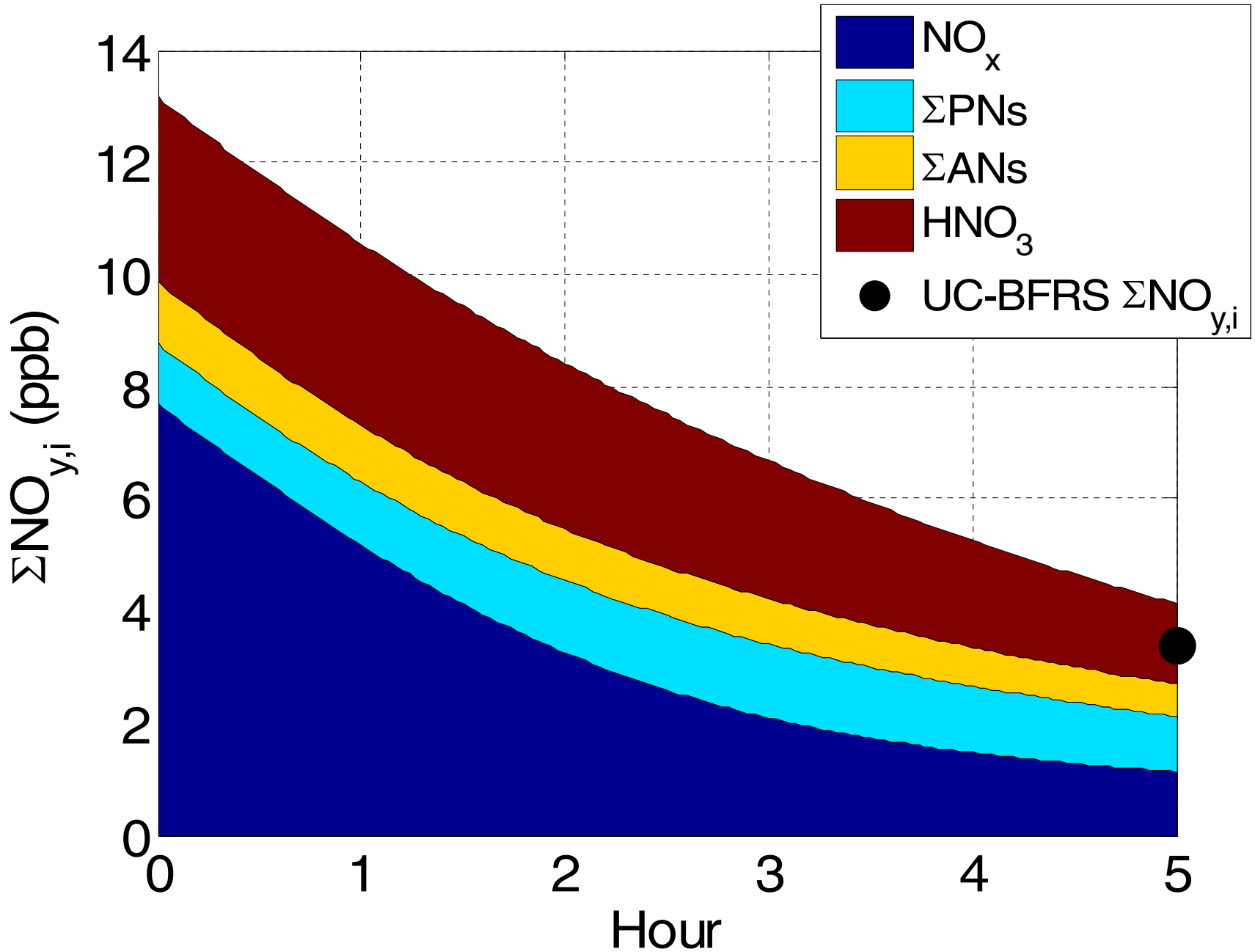
Doug A. Day, et al,
JGR., **107(D6)**, ‘02.

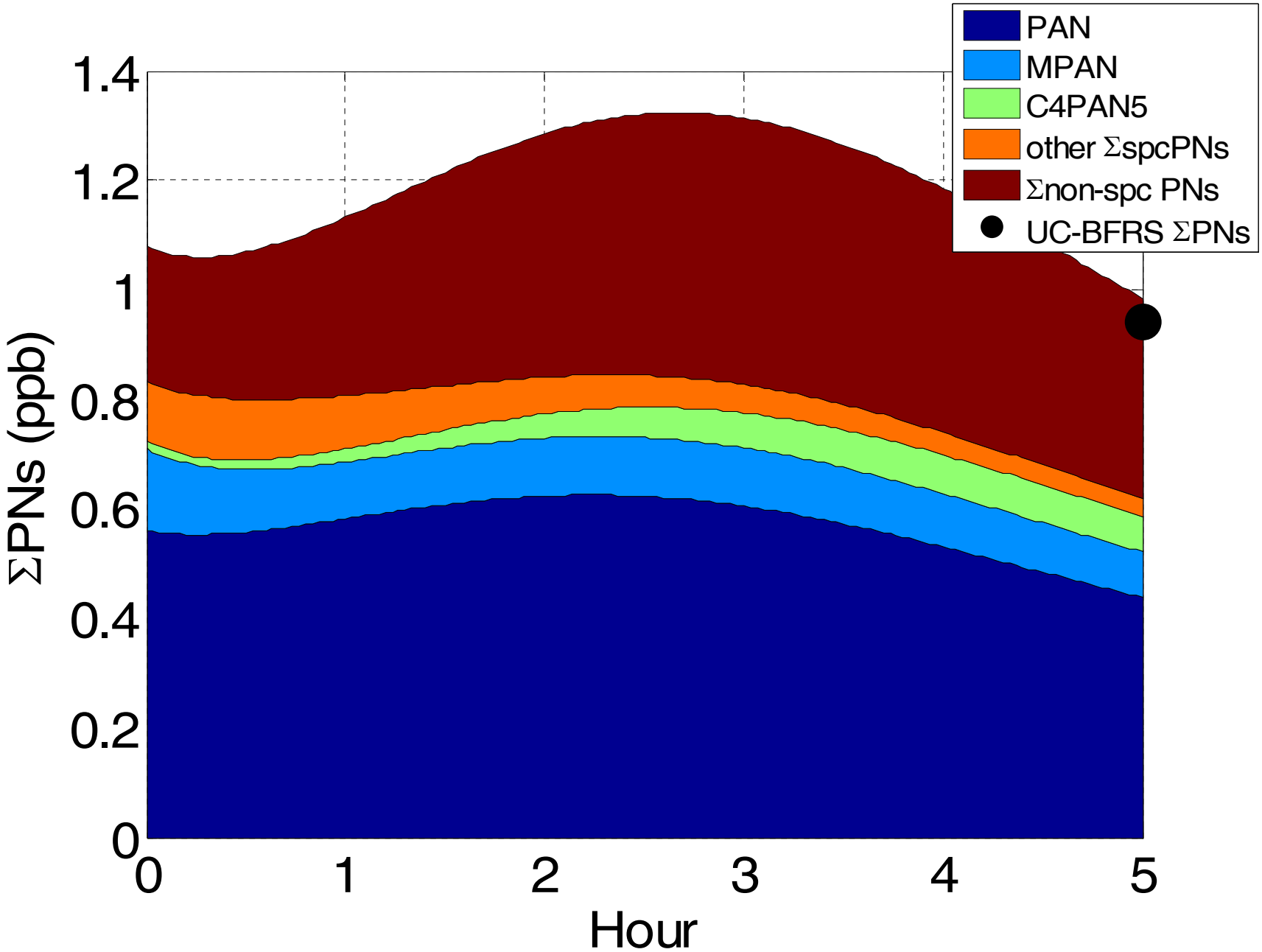

Oven 2 held at 340 °C
HNO3
Oven 2 held at 180 °C
ΣANs
(RONO2)
Oven 2 held at 40 °C
(RO2NO2)
ΣPNs
Field data
Cell 1 - Cell 2 (ppb)
Temperature of Oven 1 (°C)
0.8
0.6
0.4
0.2
0.0
-0.2
0
50
100
150
200
250
300
350
400
450
500
550
600
650

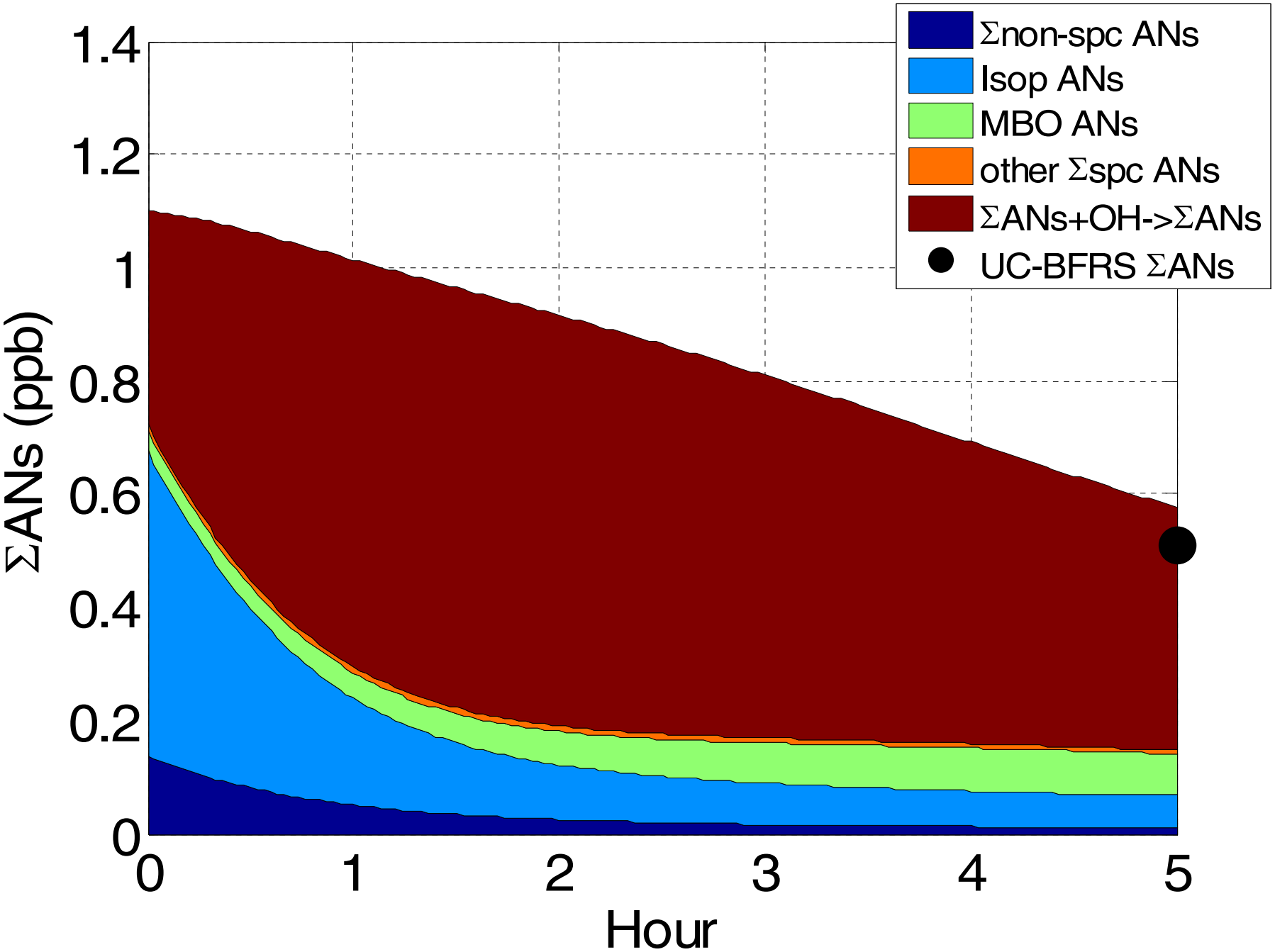
Detailed Chemical Model

- 170 individual chemicals + 7 lumped
- 350 reactions based on MCM
- Dilution with free troposphere based on long-lived tracers ~ $0.3hr^{-1}$

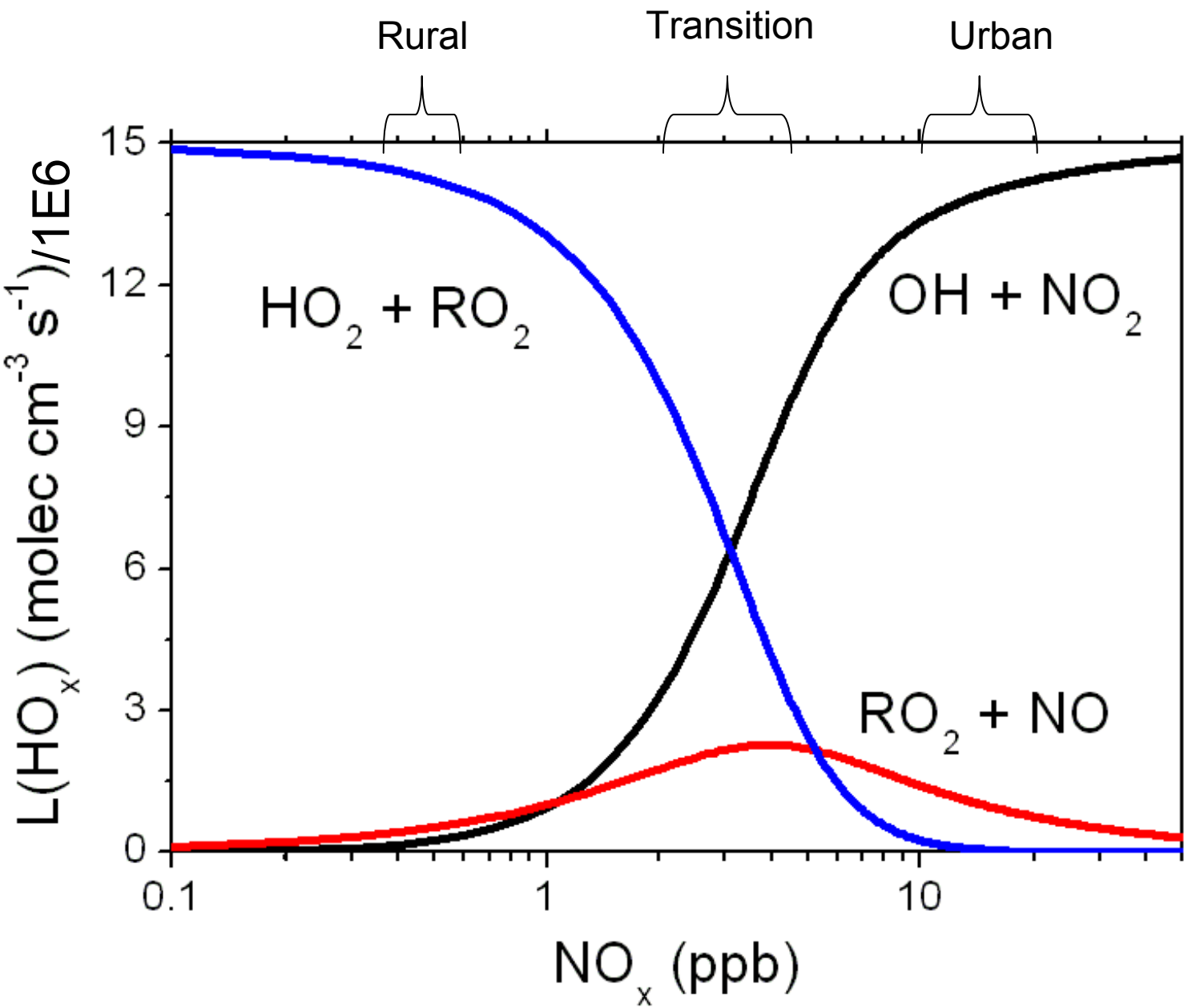

Blodgett Forest
Lake Tahoe
Folsom, Granite Bay
NIGHT
DAY
Big Hill
Sacramento


NOx
ΣPNs
ΣANs
HNO3
UC-BFRS ΣNOy,i
ΣNOy,i (ppb)
Hour
0
2
4
6
8
10
12
14
0
1
2
3
4
5

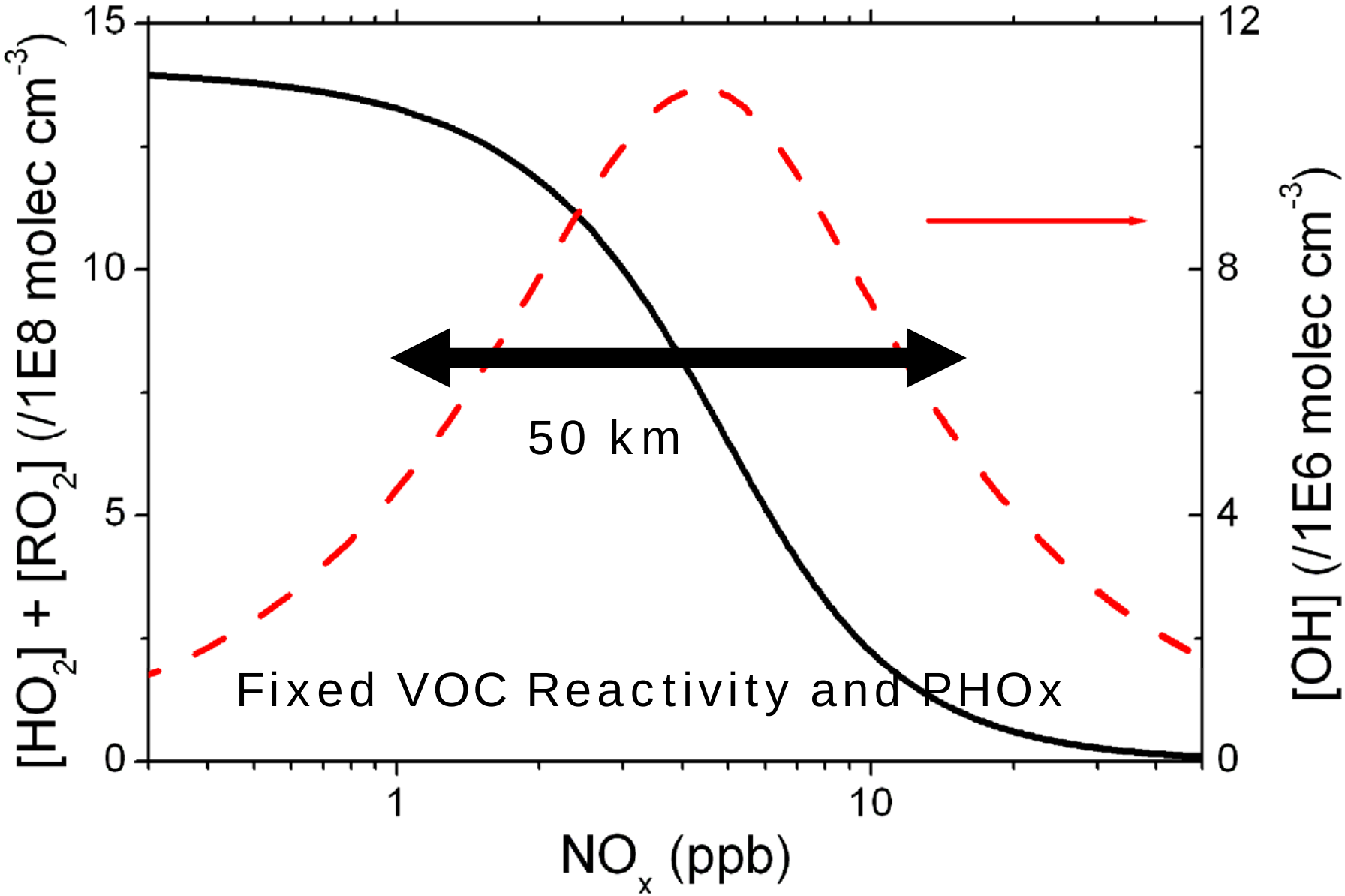

PAN
MPAN
C4PAN5
other ΣspcPNs
Σnon-spc PNs
UC-BFRS ΣPNs
ΣPNs (ppb)
Hour
0
0.2
0.4
0.6
0.8
1
1.2
1.4
0
1
2
3
4
5


Σnon-spc ANs
Isop ANs
MBO ANs
other Σspc ANs
ΣANs+OH->ΣANs
UC-BFRS ΣANs
ΣANs (ppb)
Hour
0
0.2
0.4
0.6
0.8
1
1.2
1.4
0
1
2
3
4
5

NO_x and HO_x Radical Termination



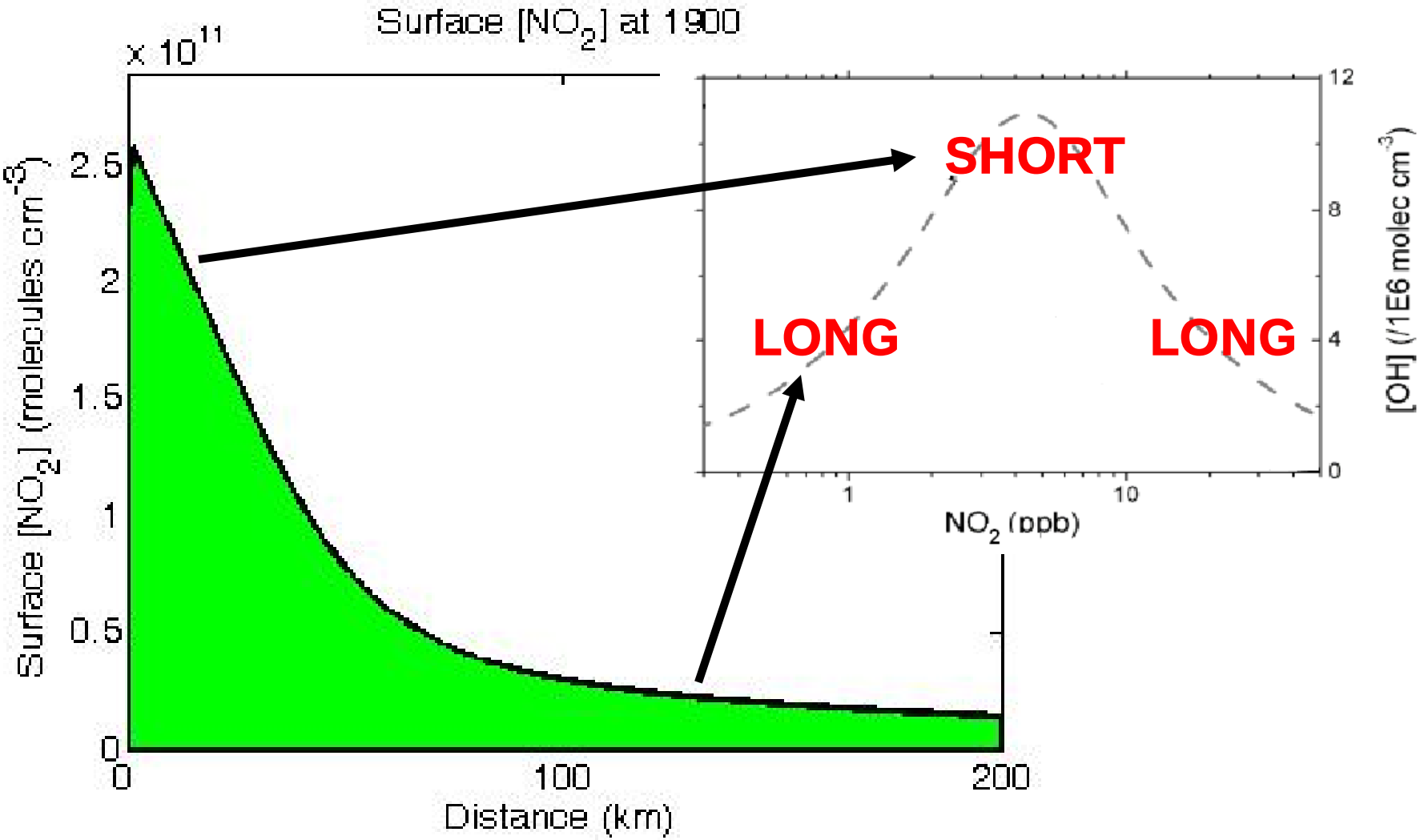
Concentrations of HO_x



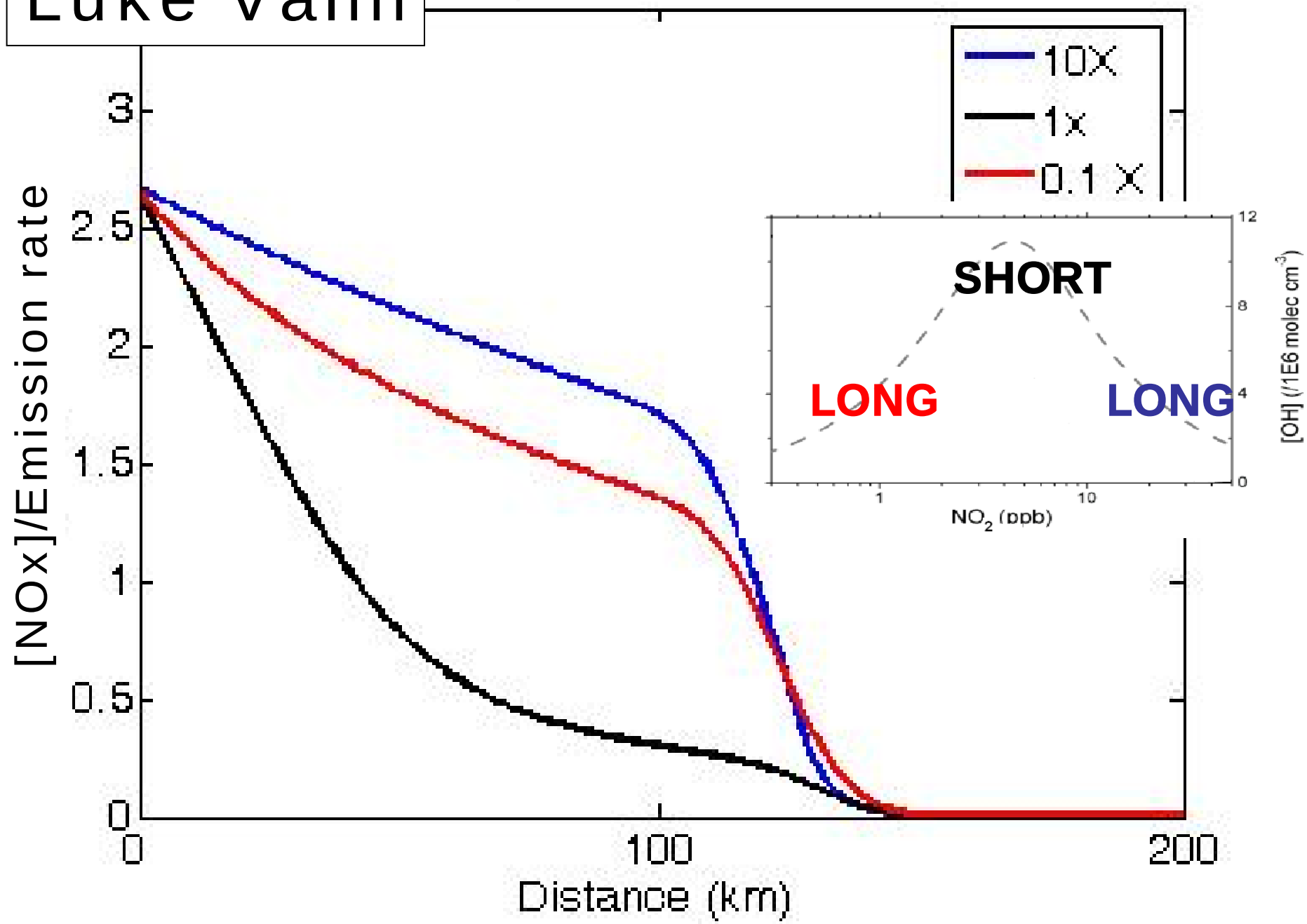
Atmospheric reactive nitrogen

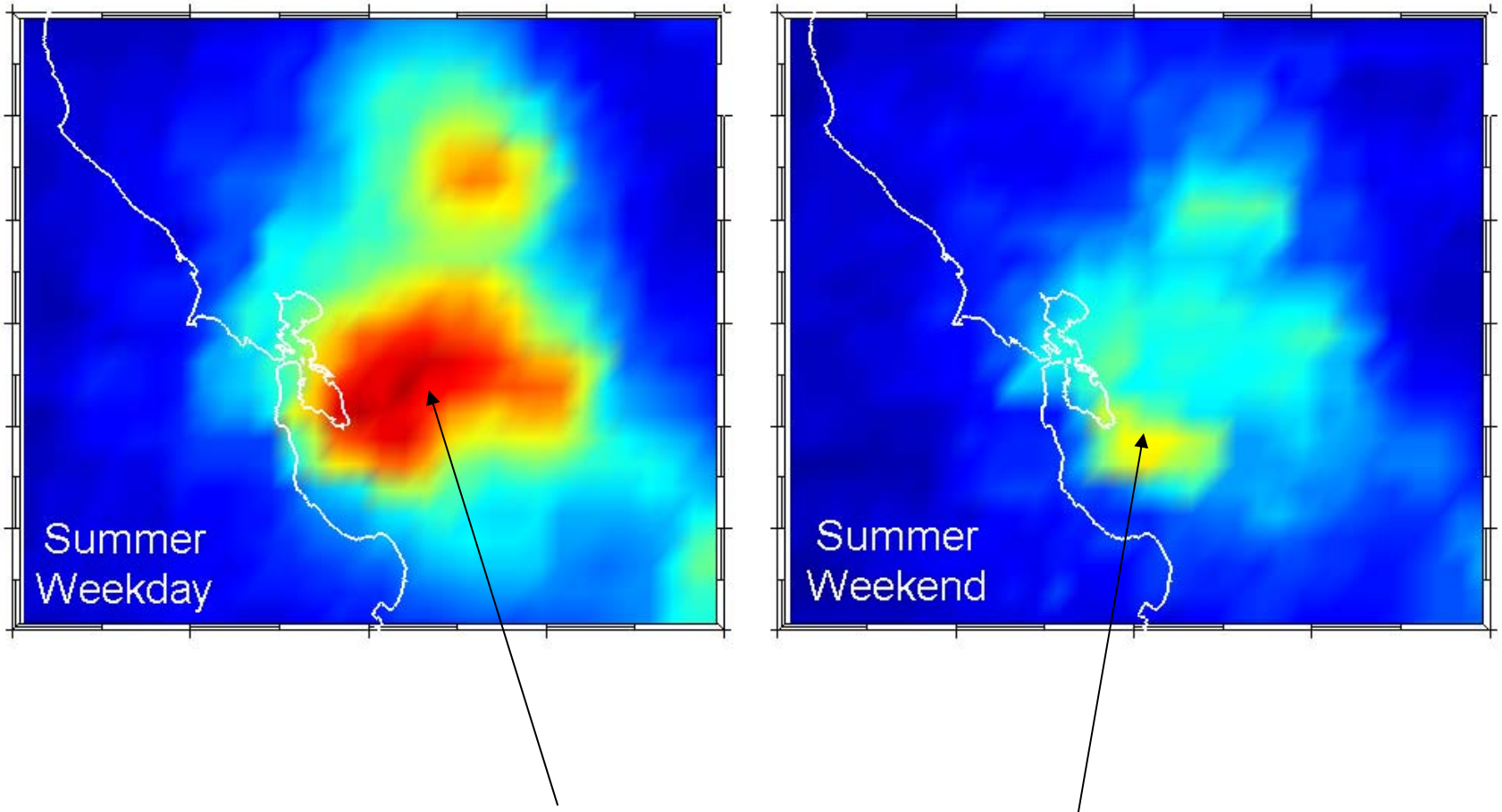
How fast is NO_x removed?

What happens to the NO_x lifetime as NO_x decreases?



Luke Valin


10X
1x
0.1 X
[NOx]/Emission rate
Distance (km)
0
0.5
1
1.5
2
2.5
3
0
100
200
SHORT
LONG
LONG
NO2 (ppb)
[OH] (/1E6 molec cm-3)
1
10
0
4
8
12

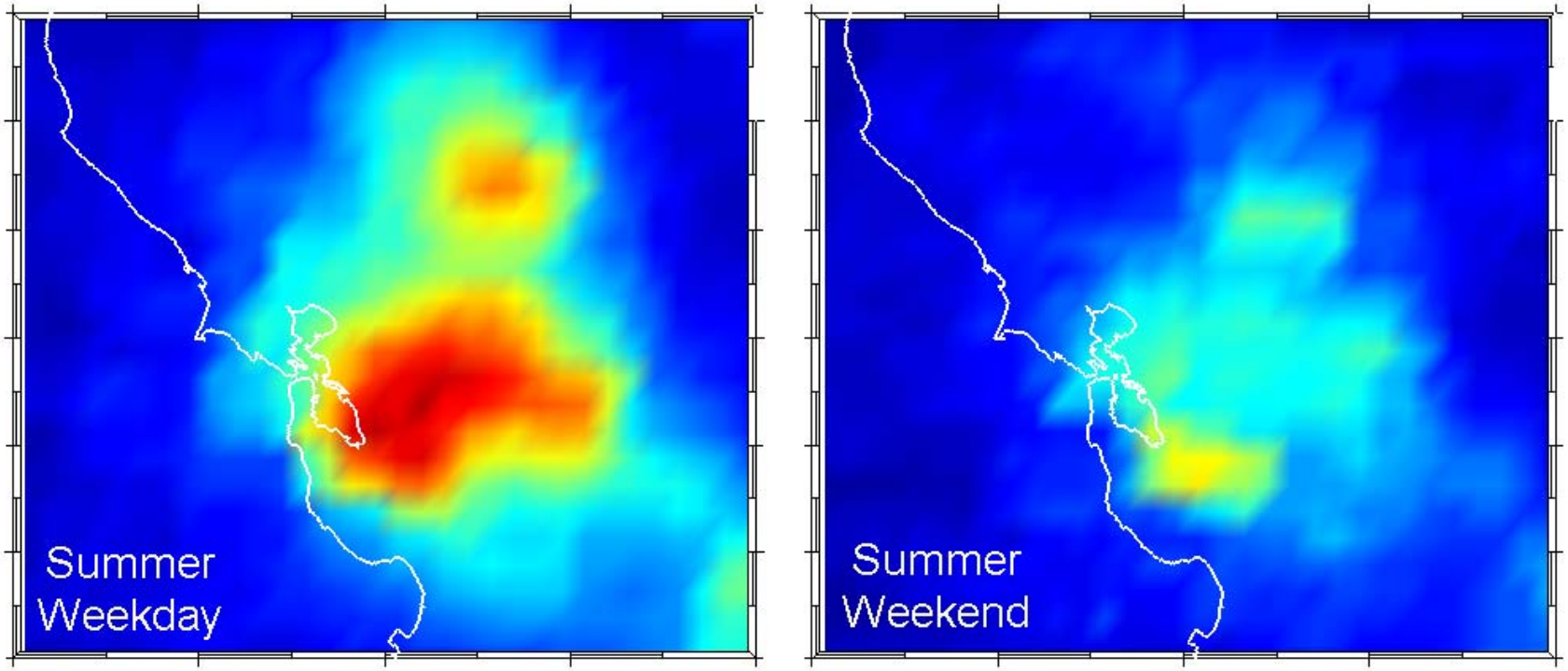


SCIAMACHY Tropospheric NO_2 Column
[molecules NO_2 cm^{-2}]

Long Lifetime

Short Lifetime

Murphy et al. ACPD **6**, 11971-12019, 2006 and **6**, 11427-11464, 2006



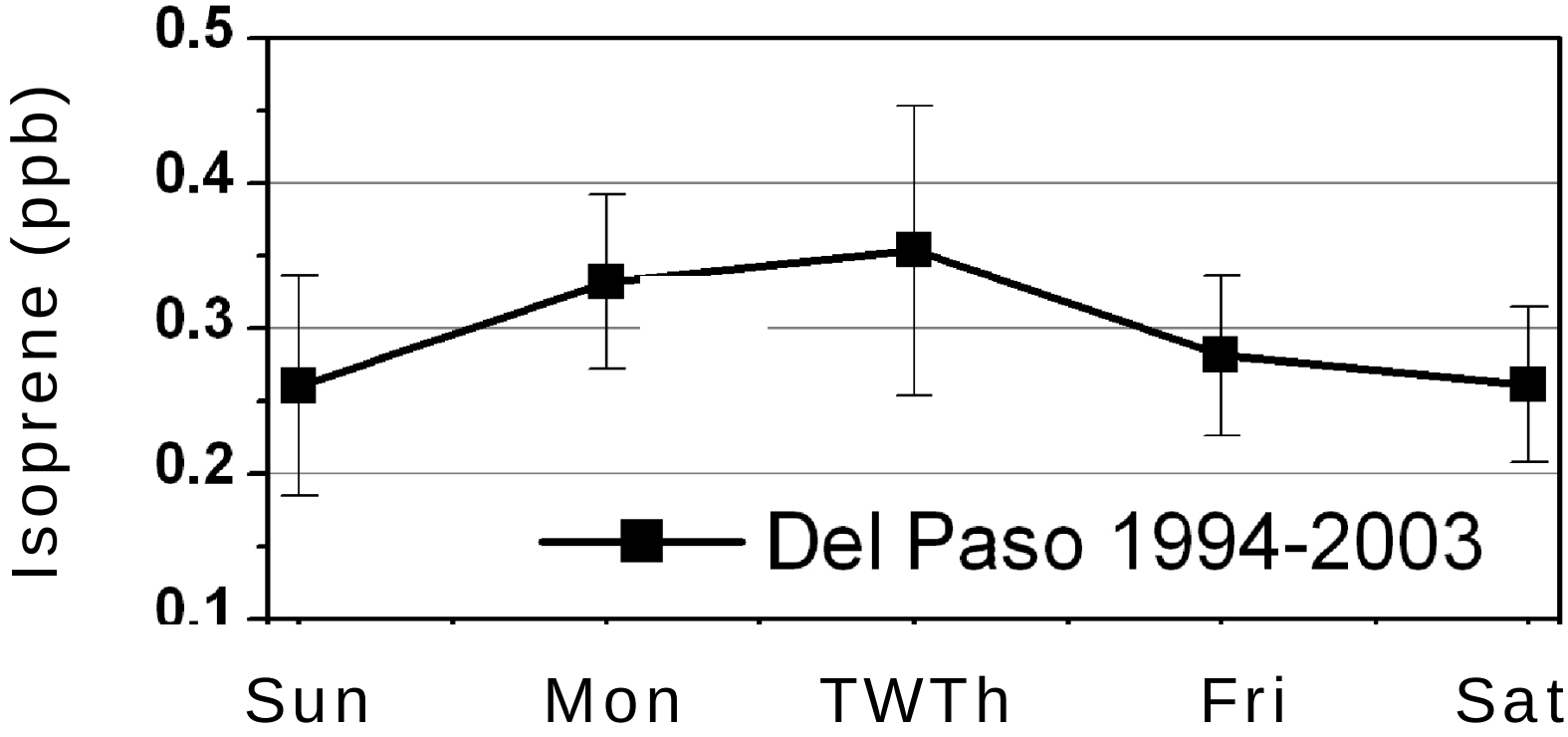
The weekend effect in NO_x causes a weekend effect in OH.

The weekend effect in OH causes a weekend effect in isoprene.

Murphy et al. ACPD **6**, 11971-12019, 2006 and **6**, 11427-11464, 2006

Urban

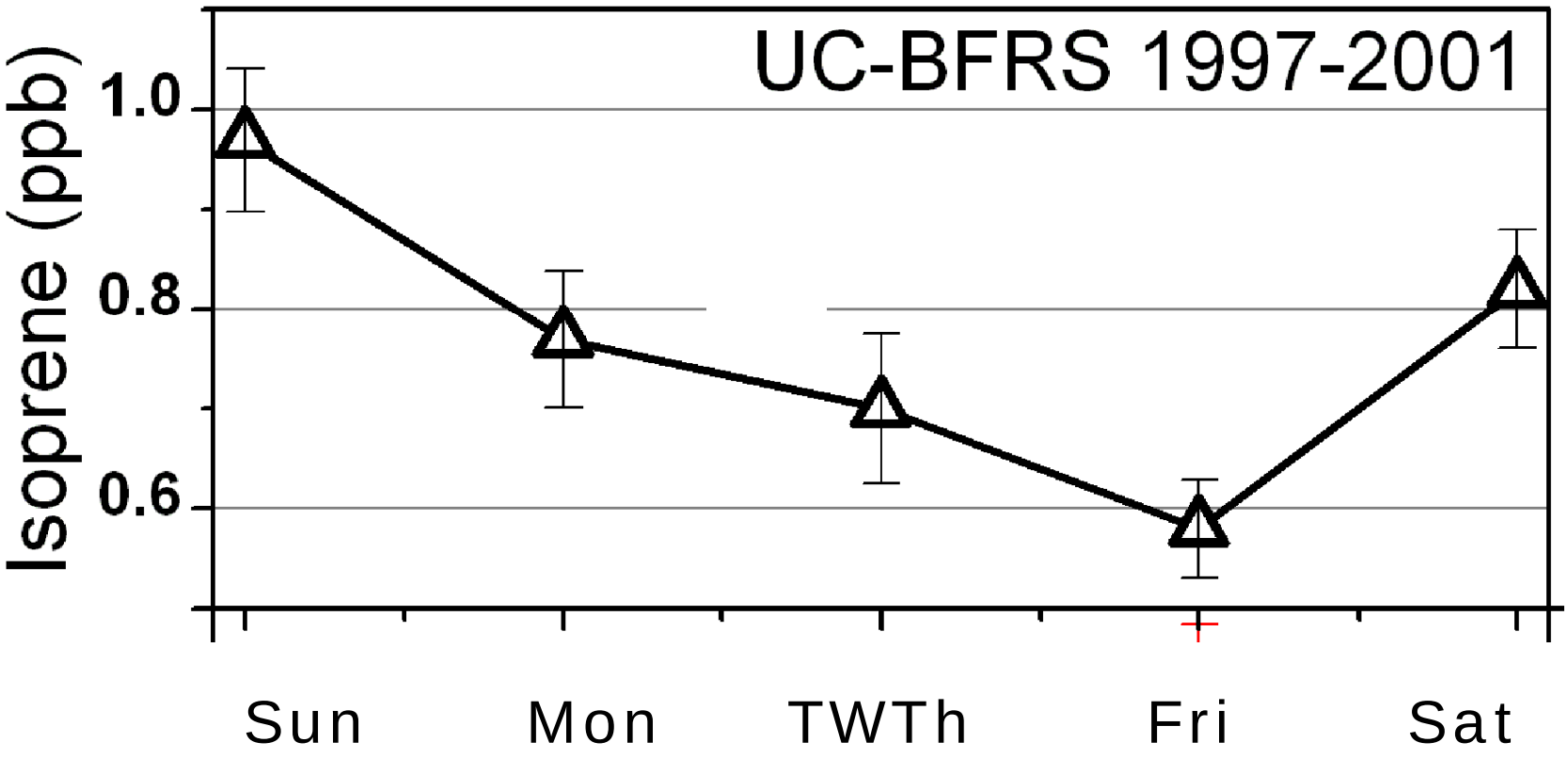
NO_x ↑ OH ↓ isoprene ↑



Murphy et al. ACPD 2006

Rural

NO_x ↑ OH ↑ isoprene ↓



The qualitative pattern of NO_x control over OH is supported by day-of-week variations in the observations of isoprene.

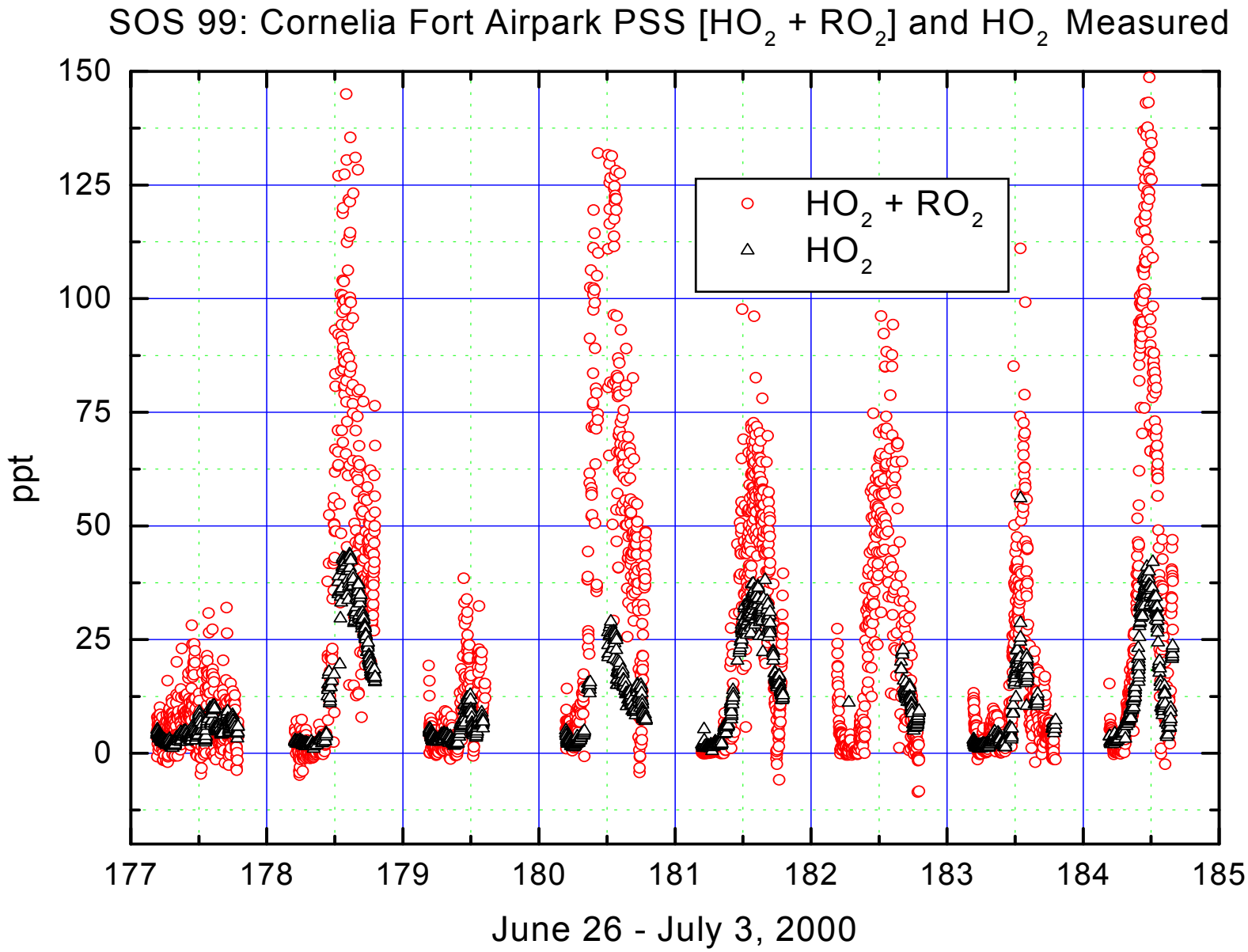
Quantitative test #1:

The HO_x Budget vs. NO_x

Joel Thornton
Now at UW Seattle

6 km from downtown
Nashville,TN

Thornton et al. JGR 107 (D12) 2002


SOS 99: Cornelia Fort Airpark PSS [HO2 + RO2] and HO2 Measured
HO2 + RO2
HO2
ppt
150
125
100
75
50
25
0
177
178
179
180
181
182
183
184
185
June 26 - July 3, 2000

Chain Termination

HO_x- HO_x

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$$

$$HO_2 + RO_2 \longrightarrow ROOH + O_2 \quad ????$$

$$HO_2 + OH \longrightarrow H_2O + O_2$$

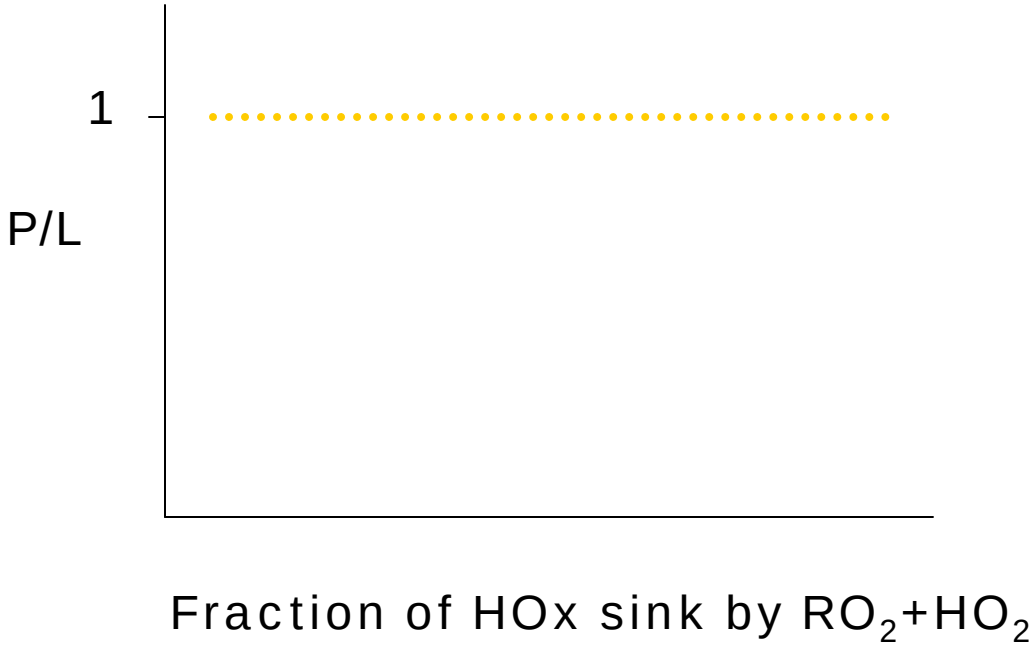
NO_x- HO_x

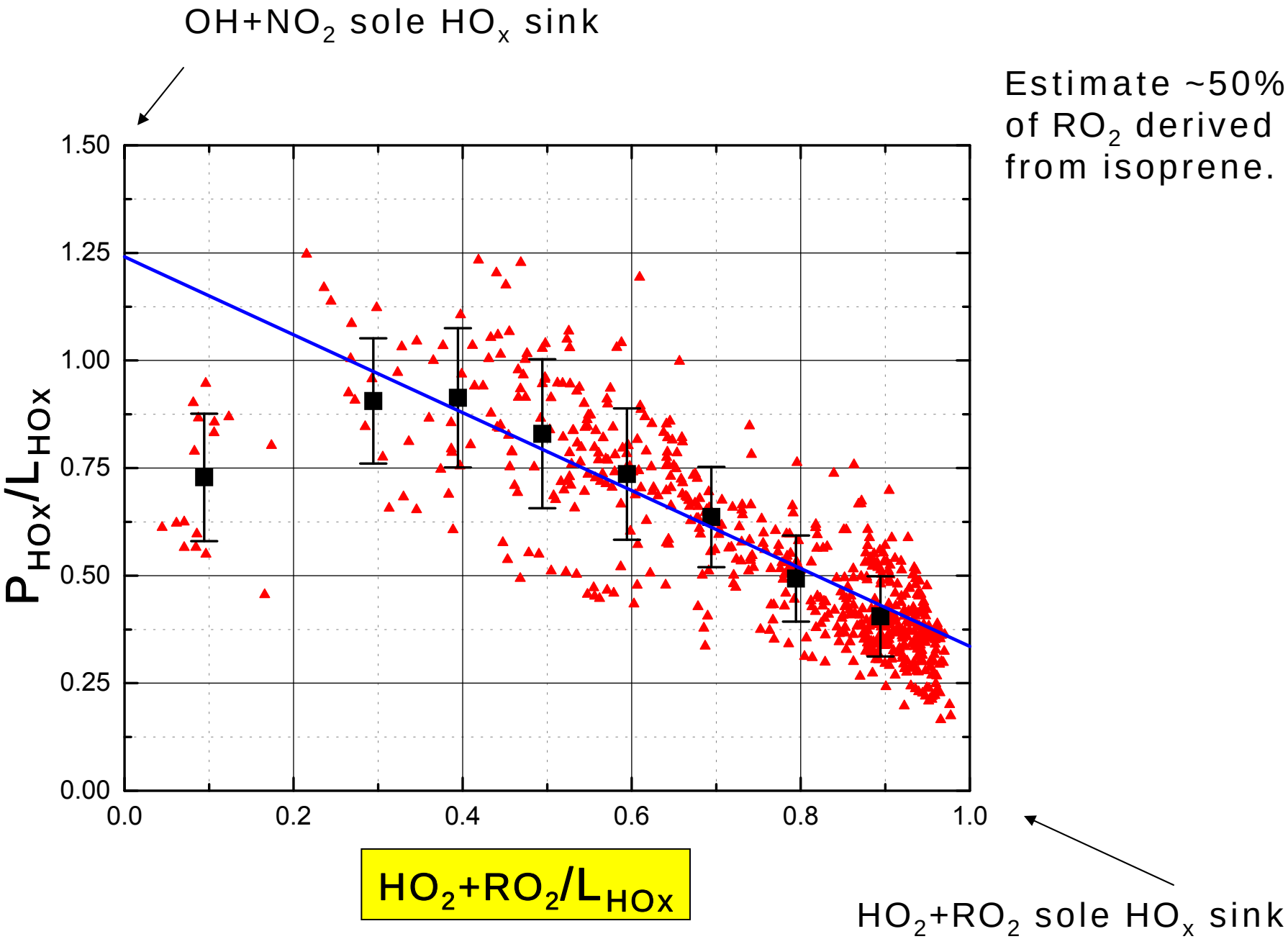
$$NO_2 + OH \xrightarrow{M} HNO_3$$

$$RO_2 + NO \xrightarrow{M} RONO_2 \quad ????$$

HO_x in steady state

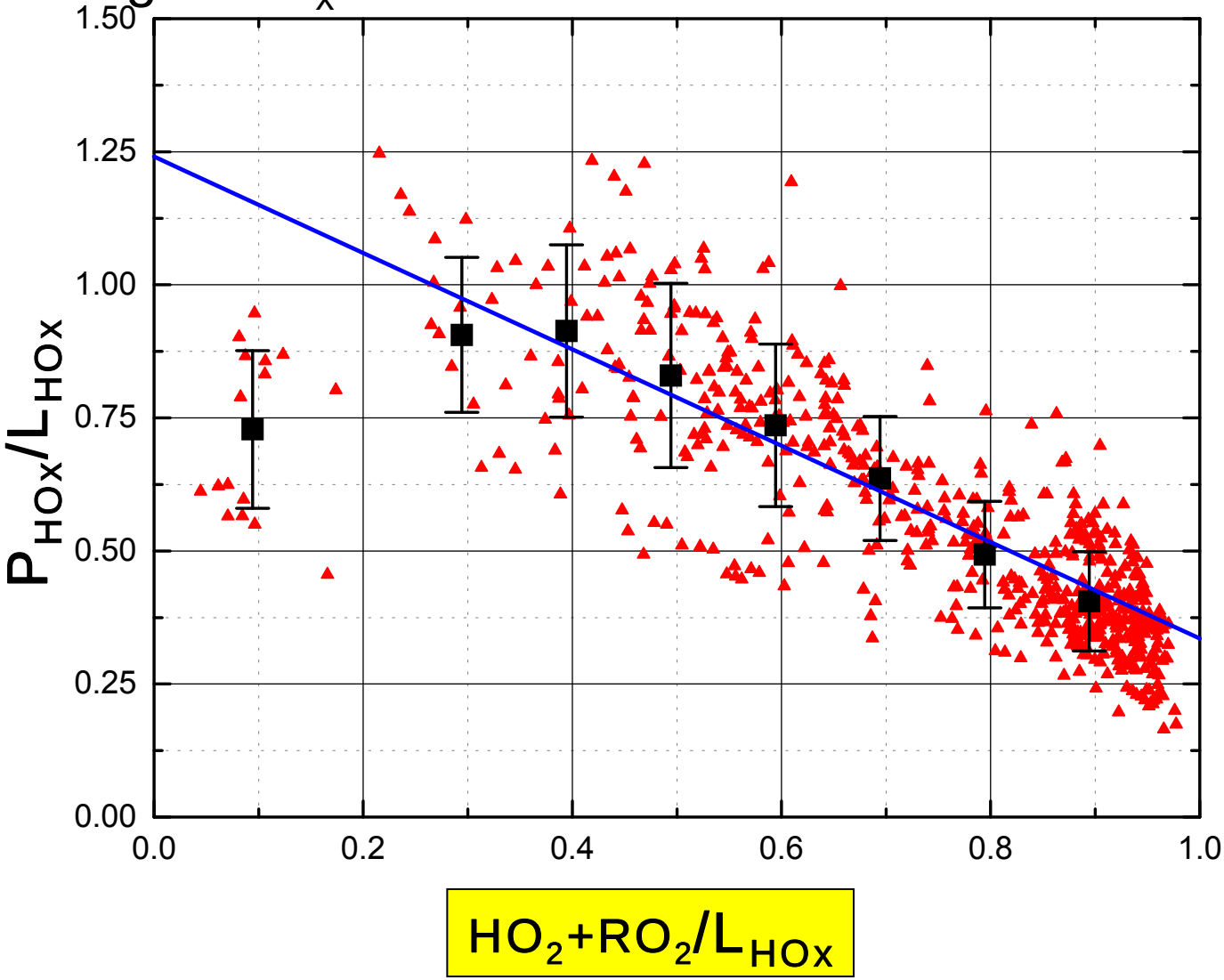
$$P_{HOx} = L_{HOx} \quad \text{or } P_{HOx}/L_{HOx} = 1$$




OH+NO2 sole HOx sink
Estimate ~50% of RO2 derived from isoprene.
1.50
1.25
1.00
0.75
0.50
0.25
0.00
PHOx/LHOx
0.0
0.2
0.4
0.6
0.8
1.0
HO2+RO2/LHOx
HO2+RO2 sole HOx sink

Urban
High NO_x

Forest
Low NO_x



Implies much more OH than in our models at low NO_x

Implication: RO_2 + HO_2 not understood

In 2002 we suggested that the products of RO_2 + HO_2 are mostly (90%) chain carriers not chain terminators, for example

$$ROOH + h\nu \rightarrow RO + OH$$

$$RO_2 + HO_2 \rightarrow RO + OH + O_2$$

$RO_2 + HO_2$ recycles OH

$$RO_2 + HO_2 \rightarrow RO + OH + O_2$$

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

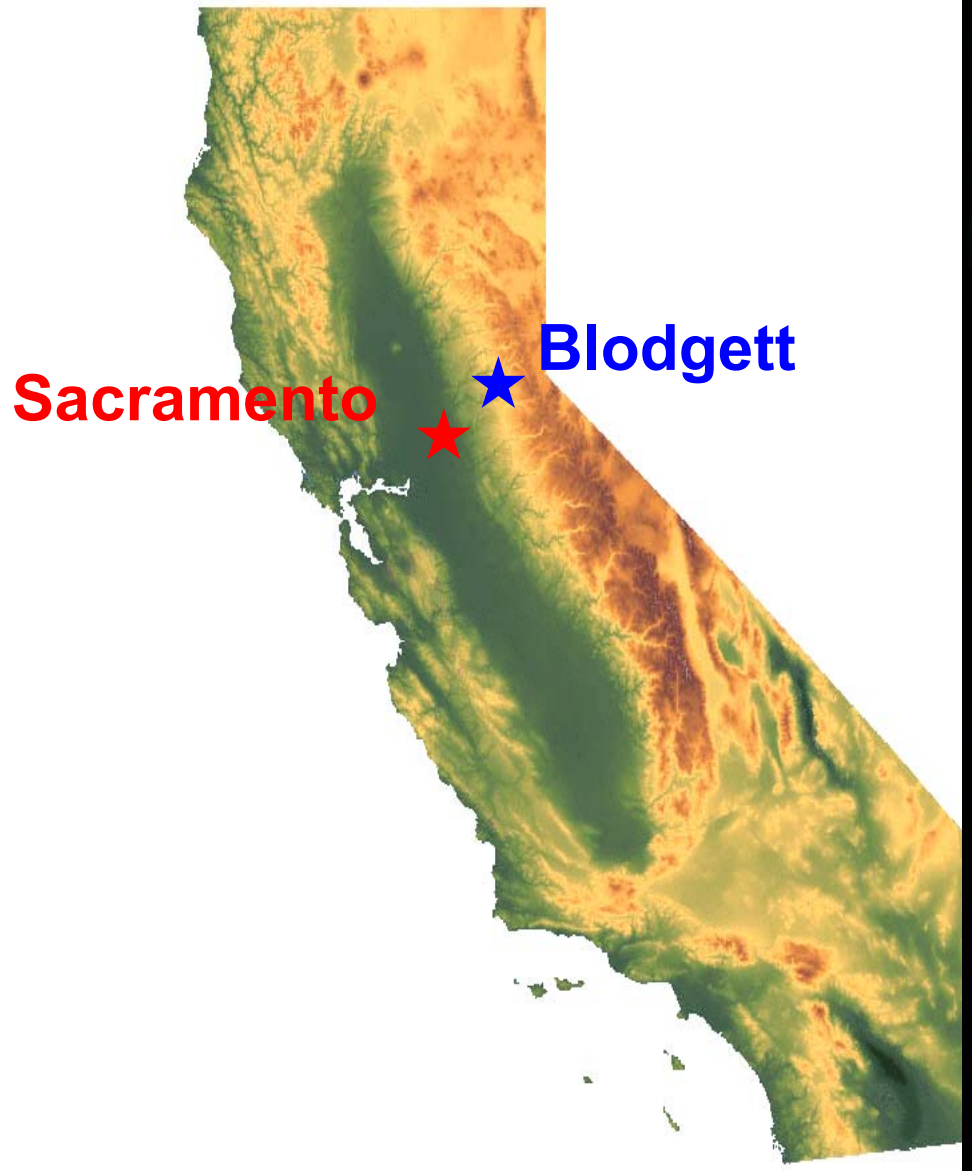
For oxygenated RO_2 radicals + HO_2 (~30-50% OH yields)

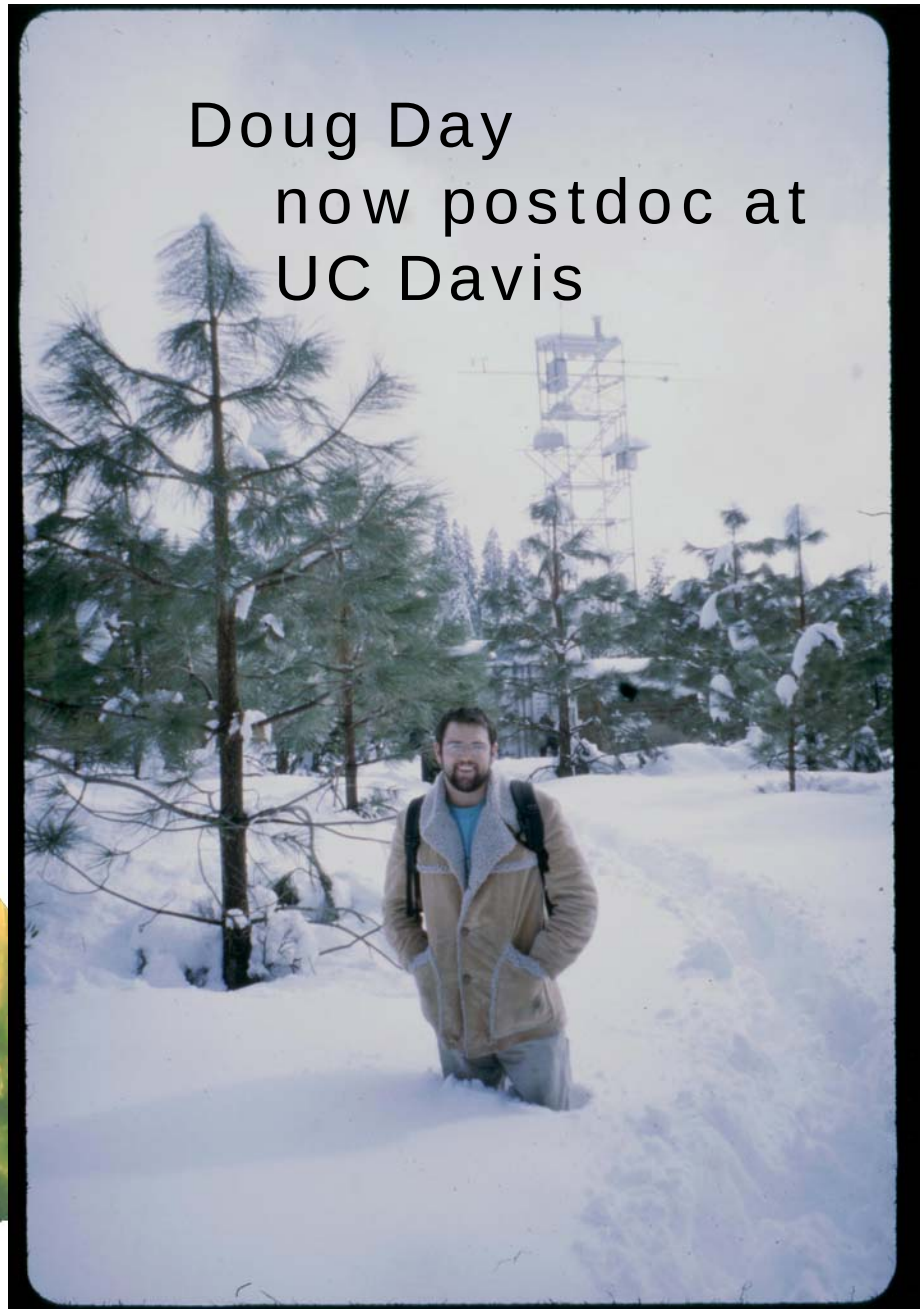
Consistent with direct measurements of OH by Penn State (Brune) and Mainz (Lelieveld) groups.

Both observe OH much larger than predicted when isoprene is high and NO_x is low.

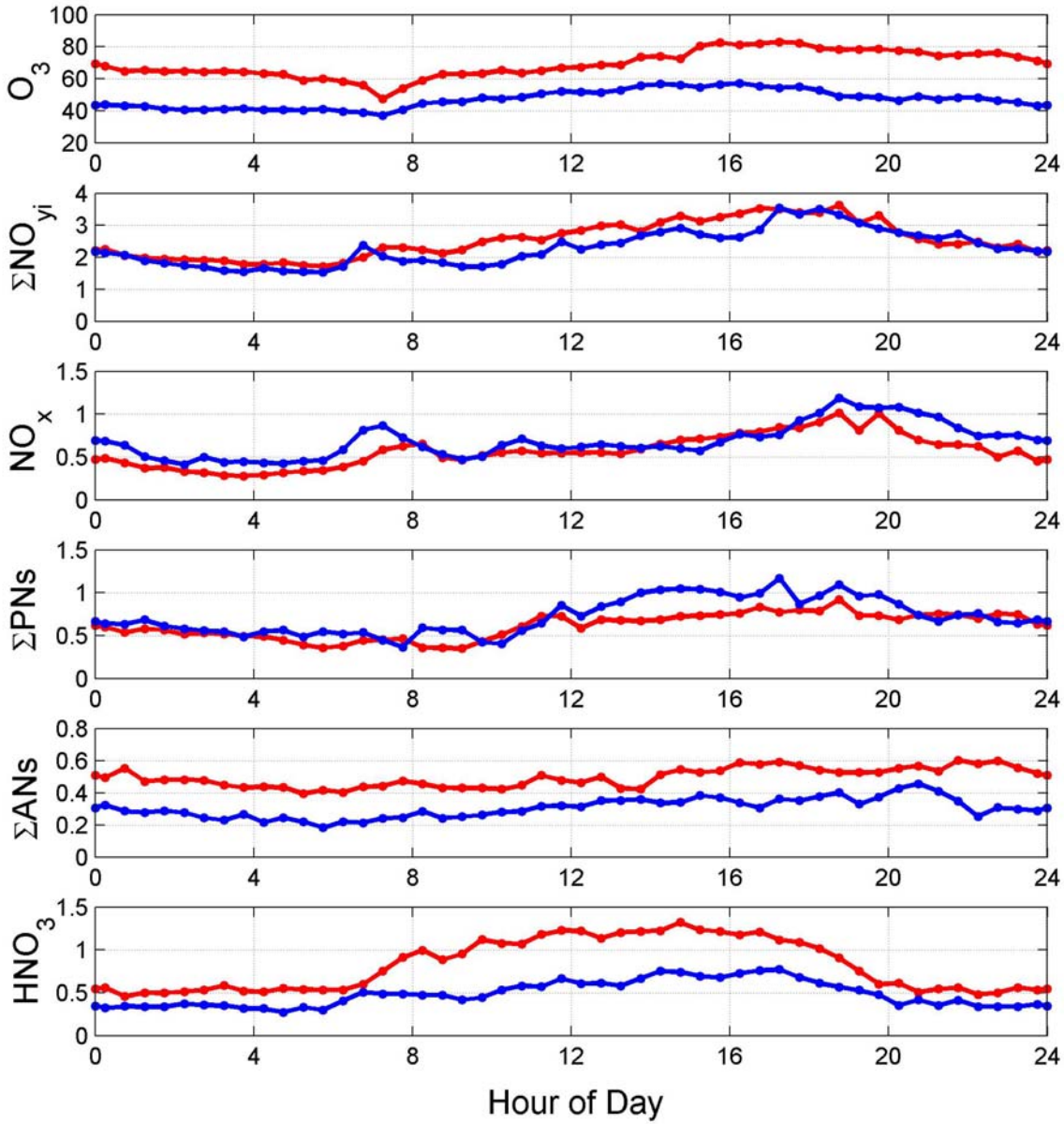
Quantitative Test #2:

HNO_3/NO_2 vs. Temperature


Blodgett
Sacramento


Doug Day
now postdoc at
UC Davis

Summer 2001: Diurnal Cycle



Red Hot (26.5°-30°C)

Blue Cold (20°-23.5°C)

Constant NO_2

HNO_3 doubles

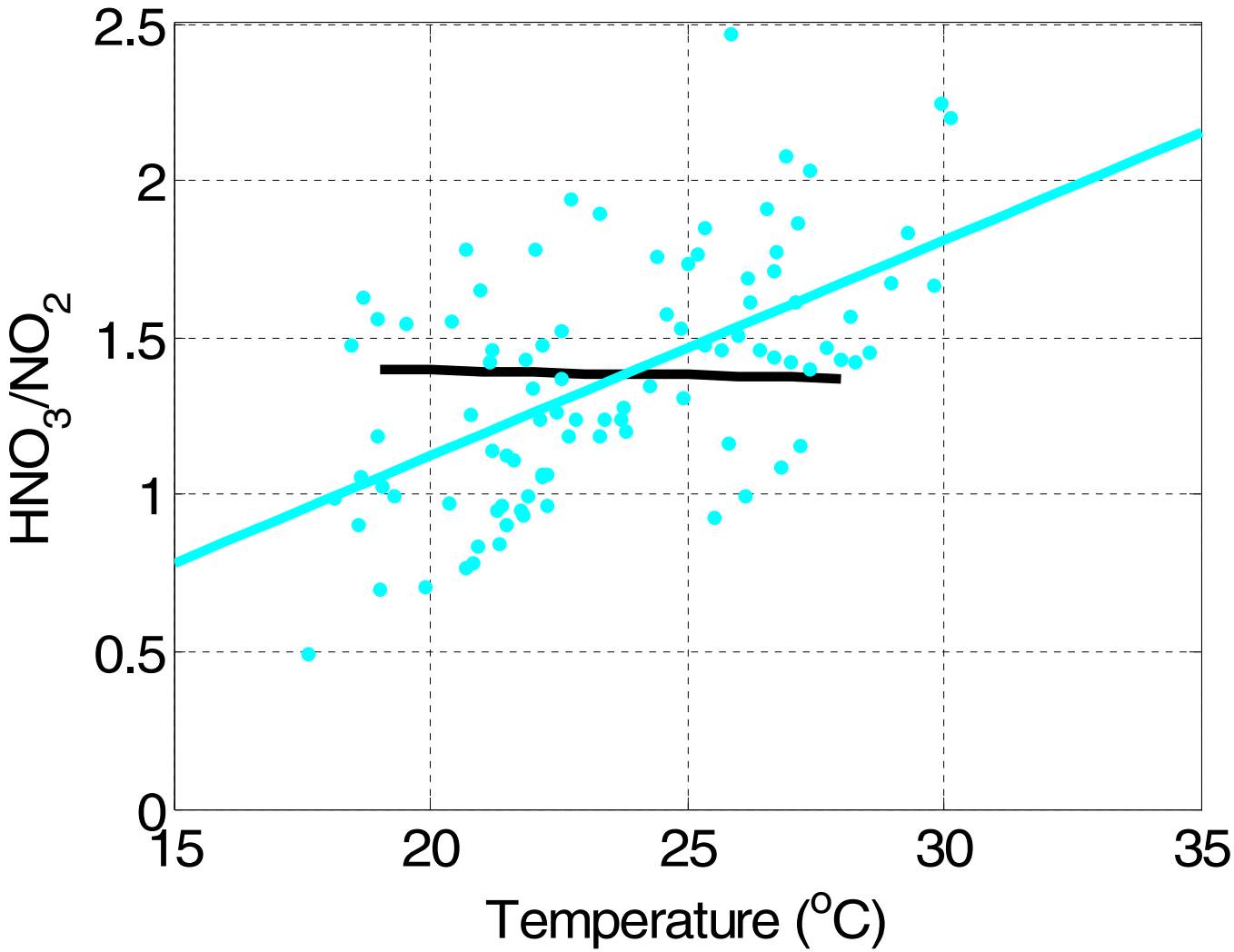
HNO_3 is in approximate steady state during the day

$P_{HNO3} = k[OH][NO_2]$

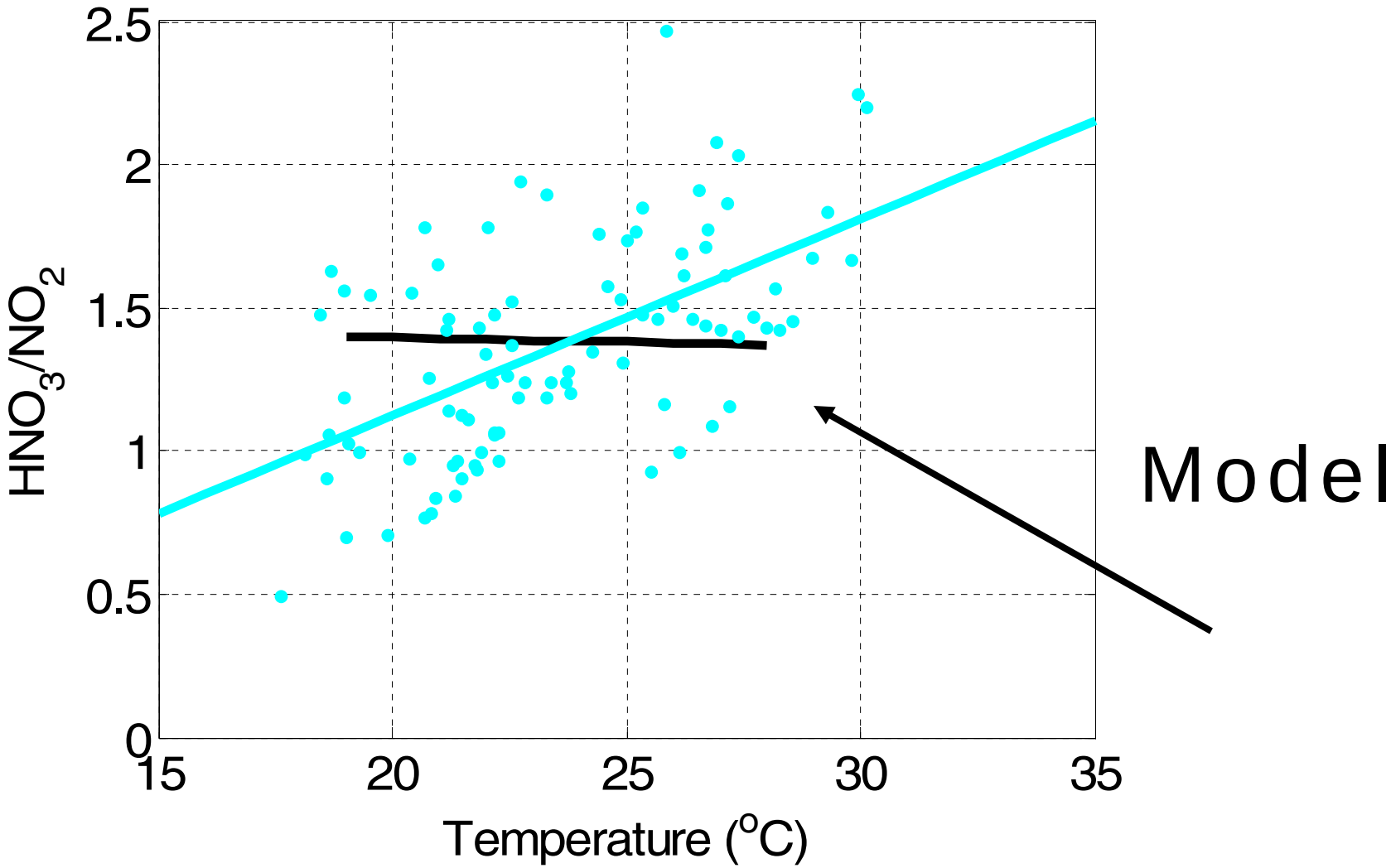
L_{HNO3} = Deposition and Mixing

$$OH \sim C' [HNO_3]/[NO_2]$$

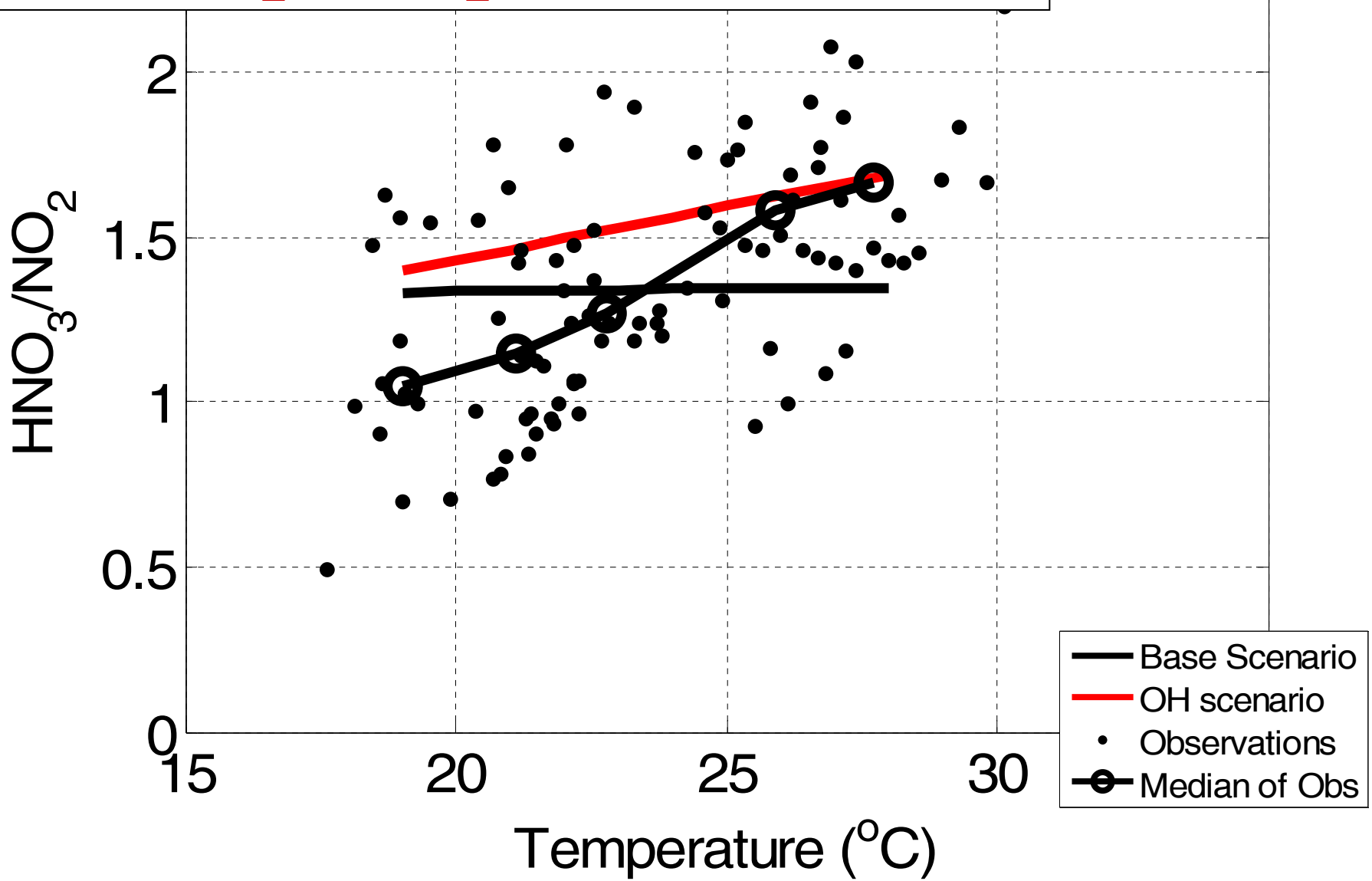
Observations imply doubling of OH with T



In contrast a detailed model with standard chemistry (Idalia Perez) has zero temperature dependence



Add a large OH Recycling For RO_2+HO_2



BEARPEX 2007 and 2009

https://webfiles.berkeley.edu/~bearpex0708/

- Fluxes and vertical gradients of NO_{yi} (Cohen, Thornton, Atlas, Wennberg)
- Detailed VOC including H_2CO, glyoxal, sesquiterpene oxidation products gradients and fluxes (Goldstein, de Gouw, Faloona, Keutsch)
- Acids and peroxides (Wennberg)
- Aerosol composition and fluxes (Jimenez, Nemitz, Vong, Covert, Goldstein)
- Direct observations of OH, HO_2 at multiple heights (Brune)

BEARPEX

1. Evidence supports excess OH at low NO_x

2. Evidence supports additional T-dependent OH

3. Evidence for within canopy OH is mixed. Lower T in 2007 season?

See special issue to come in Jan 2009 or so

Implications:

Faster chemistry in a warmer climate!!

Low NO_x coupling to HO_x wrong in all current models! RO_2 + HO_2 chemistry can now be fixed.

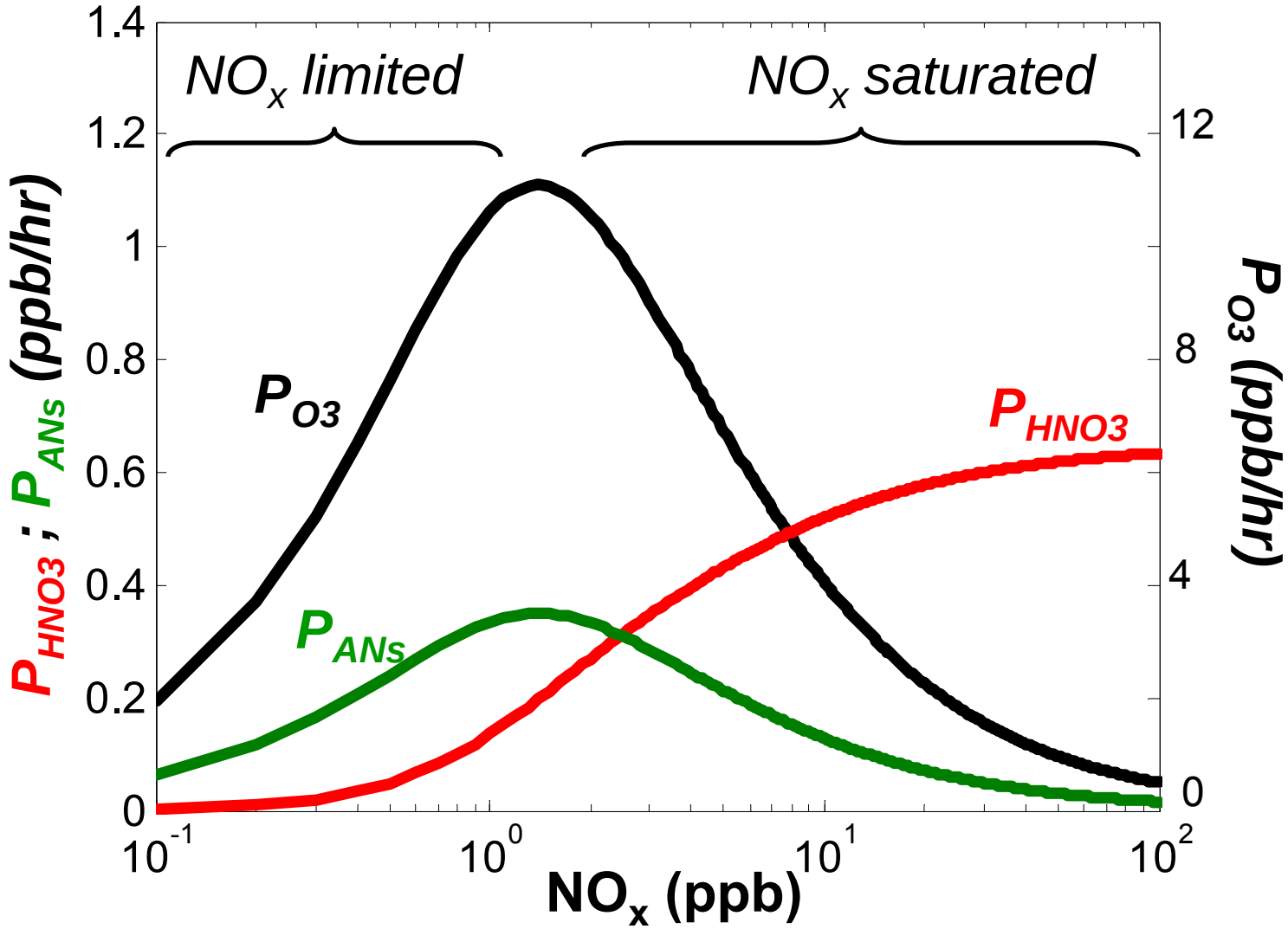
What other N-related chemistry of biogenics is poorly understood?

$RONO_2$?

Secondary Aerosol?

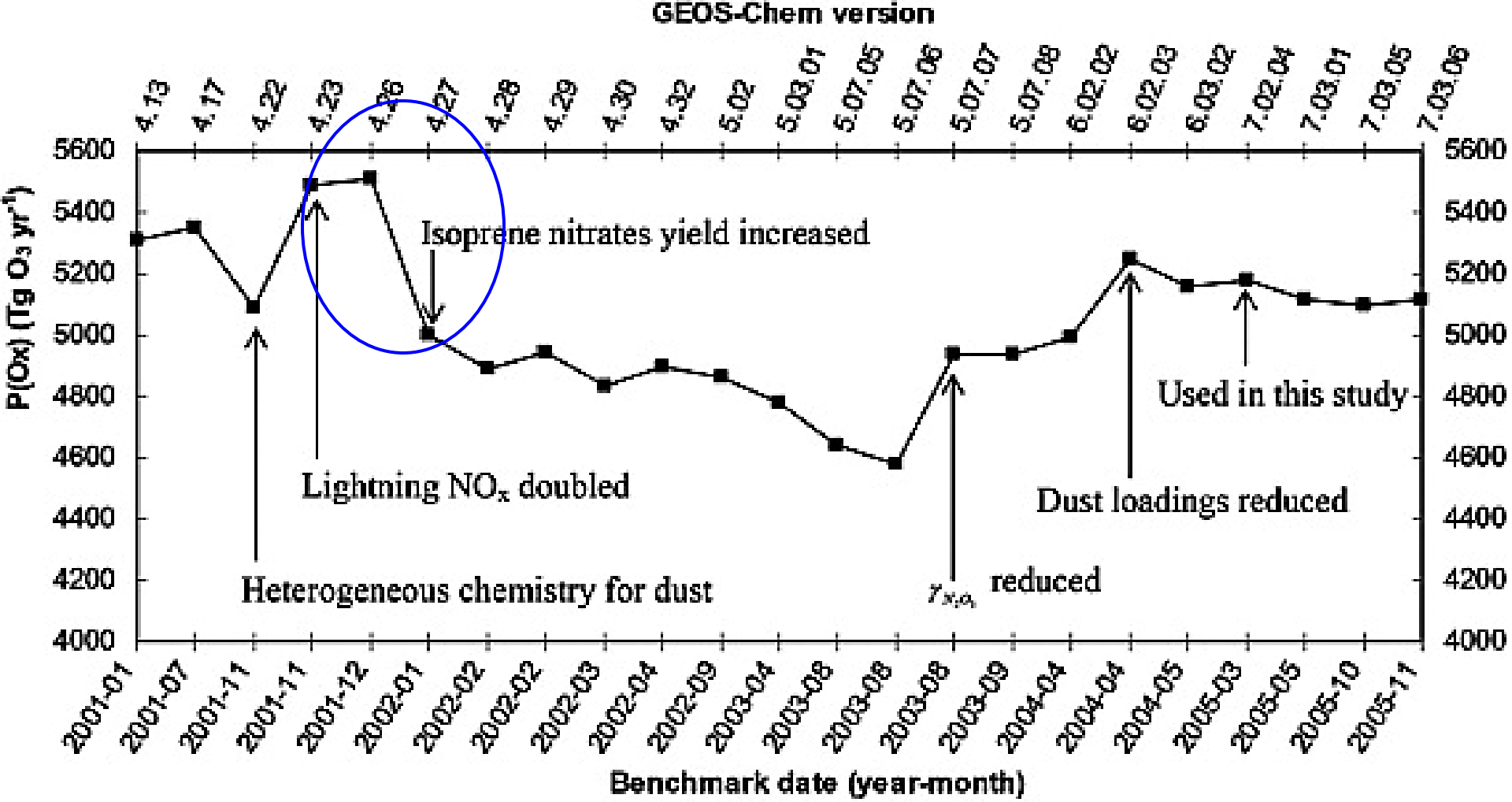
$RONO_2$

$RONO_2$ significant, often ignored



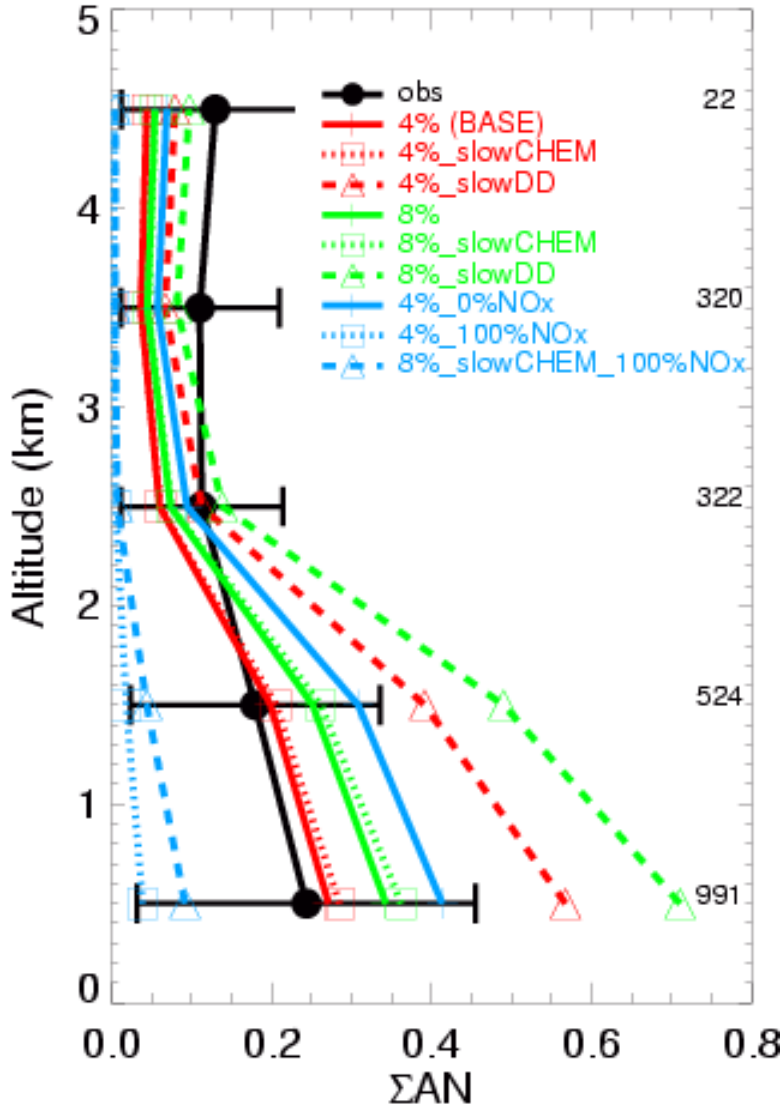
- $RONO_2$ formation (especially form isoprene and other biogenics) is one of the key uncertainties in future AQ.

- Models with high $RONO_2$ production remove NO_x faster than they increase O_3 when isoprene emissions grow.



Wu et al, 2007

A ~10% change in global O_3 when isoprene branching ratio was changed from 4.4% to 12%.

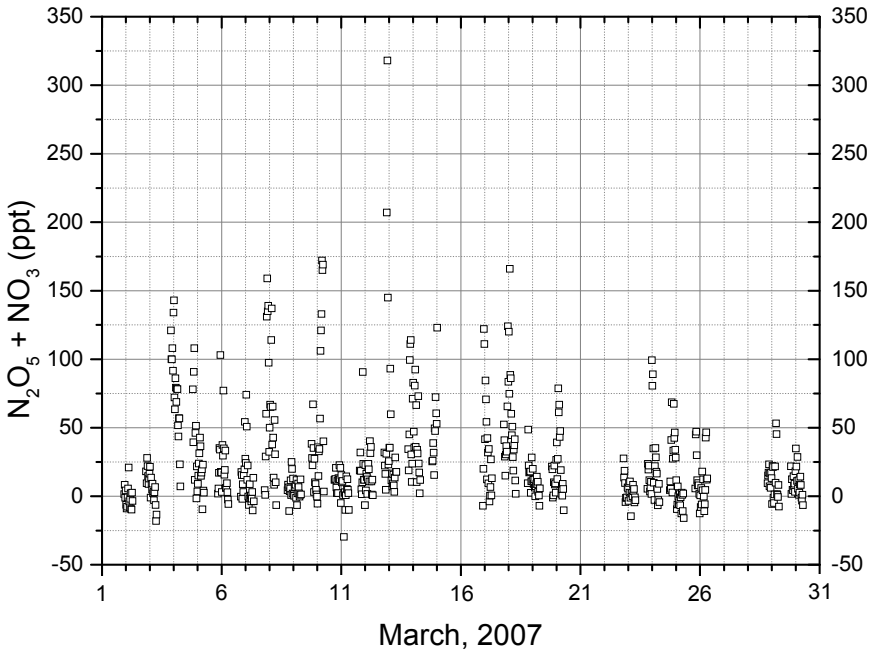


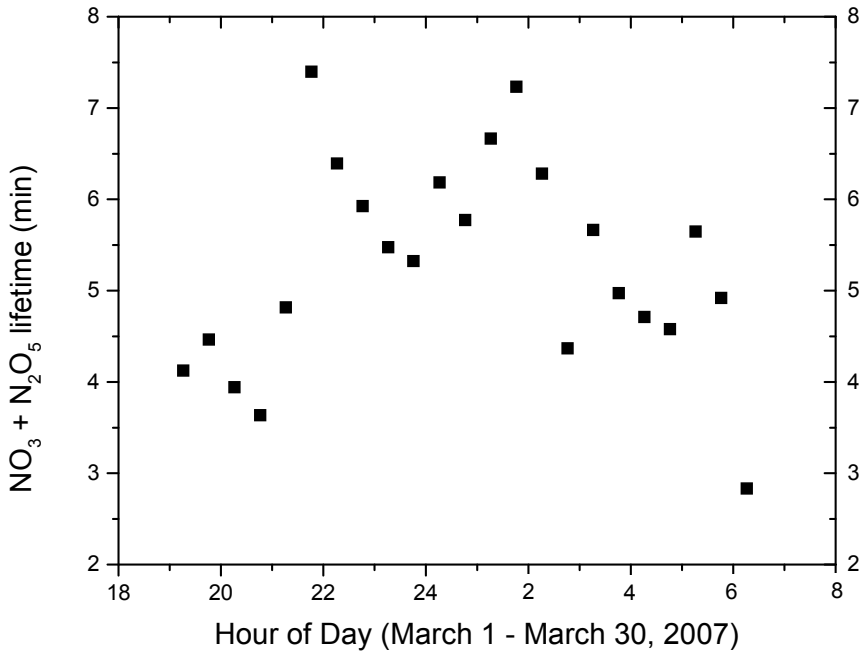
Our aircraft observations and a global model:

Horowitz et al, JGR 2007.

Found smaller branching ratio more consistent within their mechanism.

NO_3 and N_2O_5 Chemistry

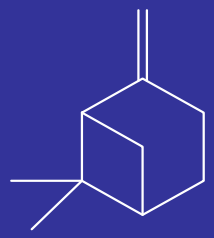




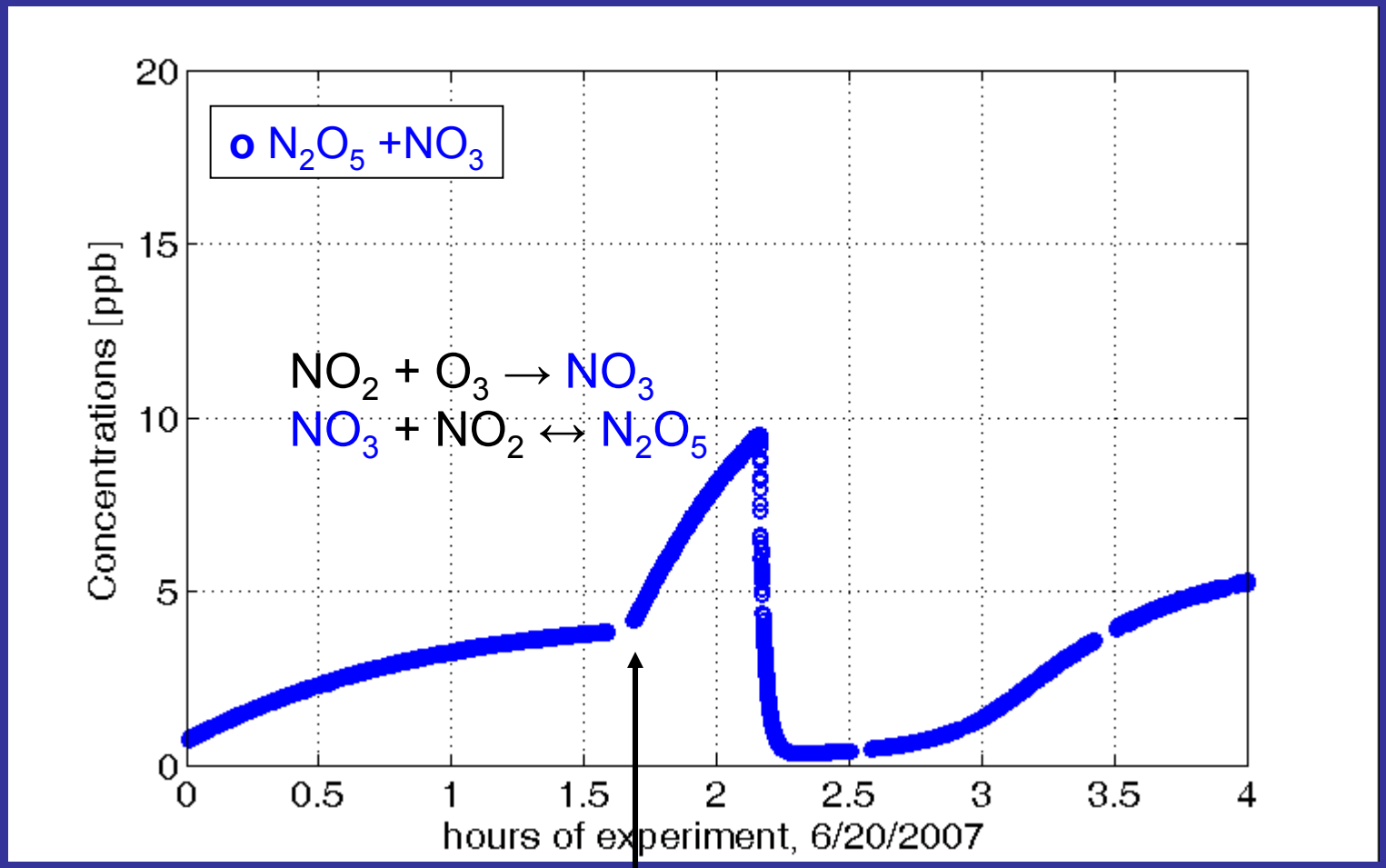
In the PBL NO_3 reacts with VOC

- N_2O_5 chemistry on aerosol as a source of aerosol nitrate is not important near the surface.
- The fate of NO_3 after it reacts with VOC is poorly tracked if at all—and no observations provide strong constraints.
- This chemistry is a major sink of O_x unless the $RONO_2$ formed is recycled to NO_2 in the daytime.

Aerosol chemistry: NO_3 + β-pinene in the SAPHIR Chamber

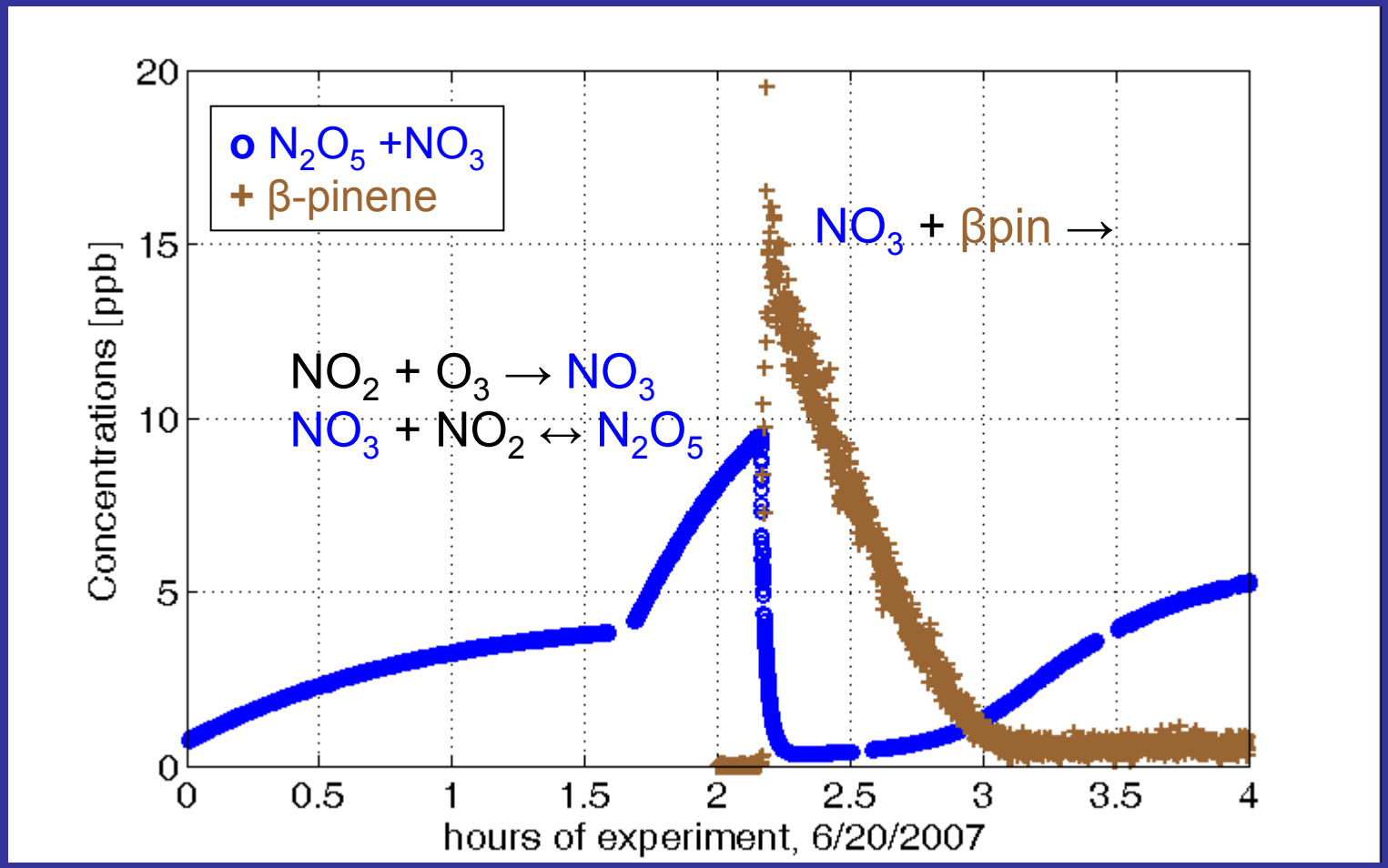


Observed kinetics: nitrate formation

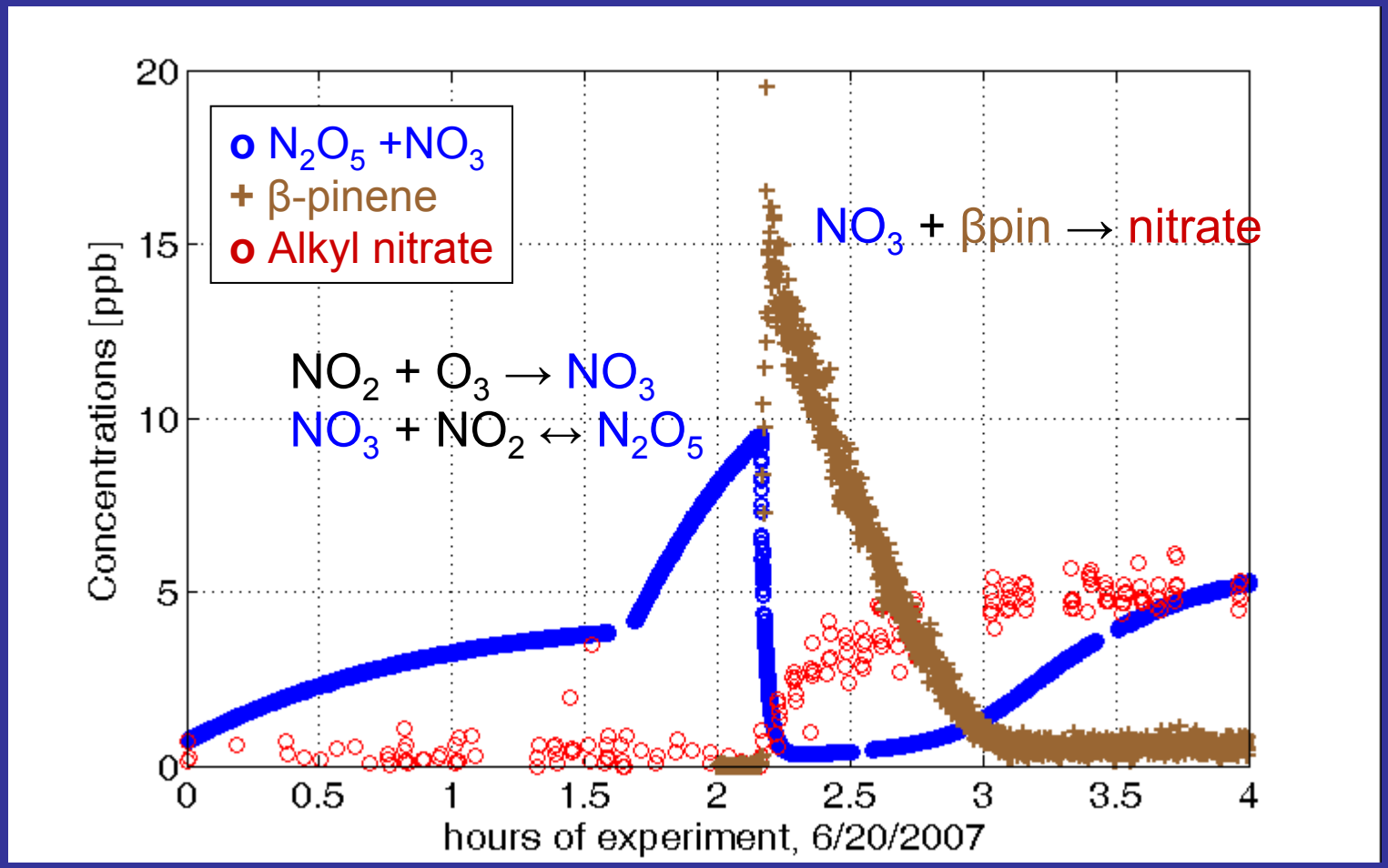


2nd re-charge injection of O_3

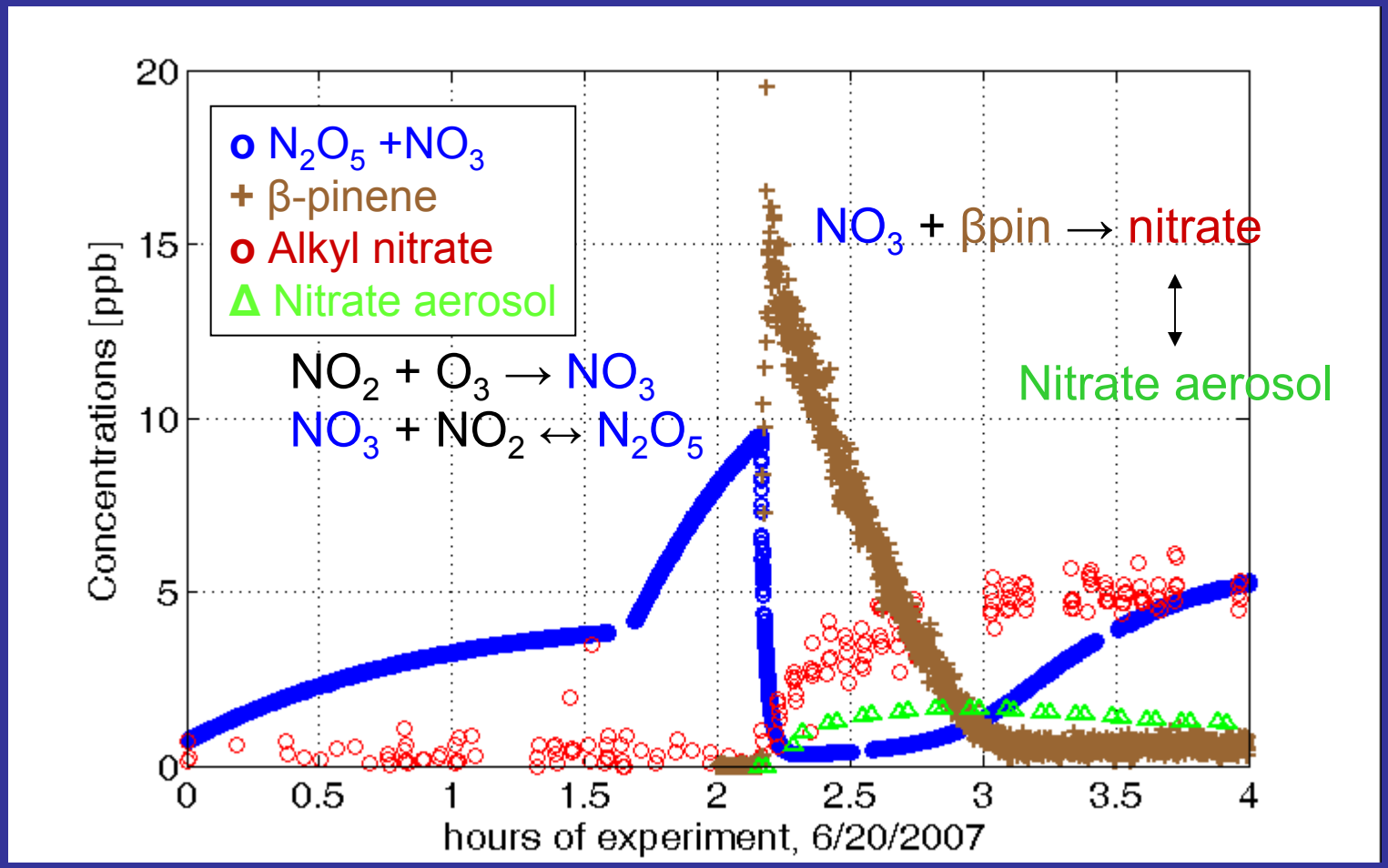
Observed kinetics: nitrate formation



Observed kinetics: nitrate formation

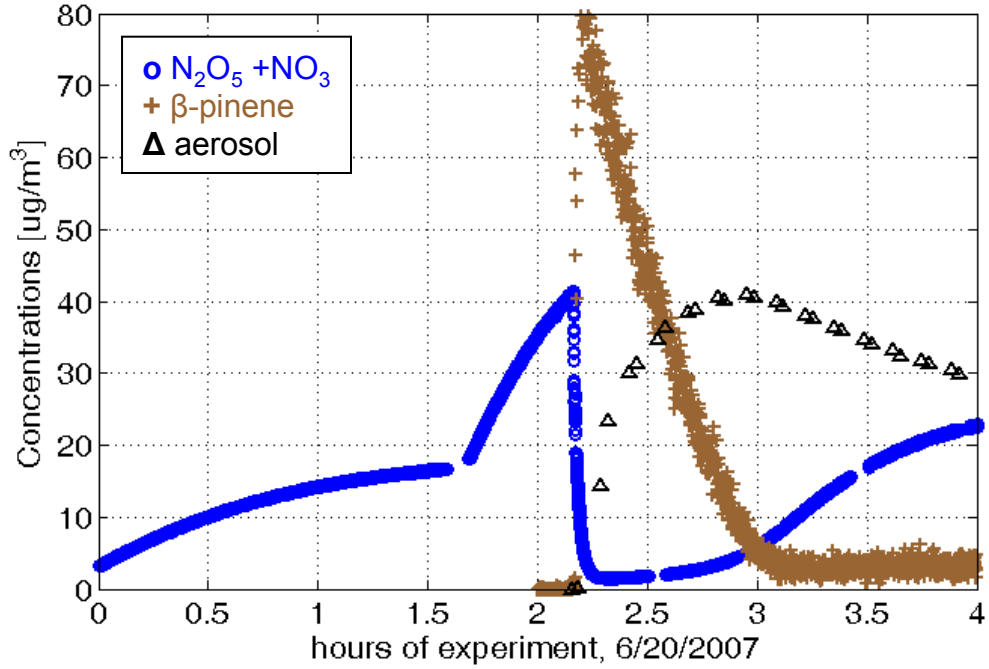


Observed kinetics: nitrate formation



aerosol formation

DRY

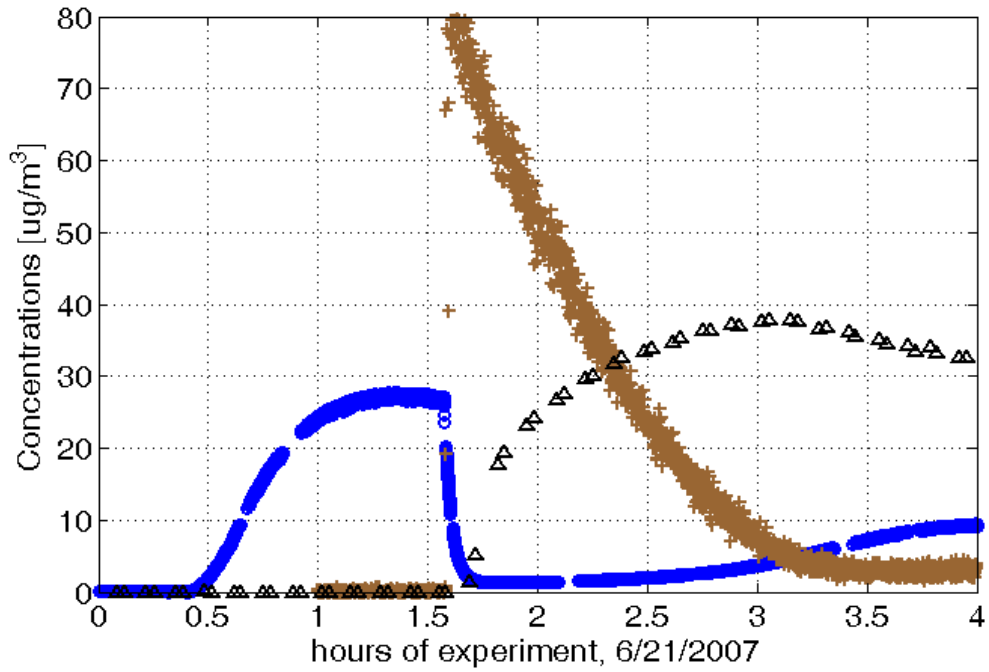


Y~40%

$$Y = \frac{\Delta M_{aero}}{\Delta HC}$$

(corrected for wall losses)

60% RH



Y~50%

How much aerosol could NO_3 + β-pinene make globally?

- Mass yield of aerosol from NO_3 + β-pinene: ~50%

- Global β-pinene emissions: ~ 33 Tg yr^{-1}; ~30% at night

- Fraction of nighttime β-pinene that reacts with NO_3, based on relative NO_3 (1 ppt), O_3 lifetimes (60 ppb): ~ 70%

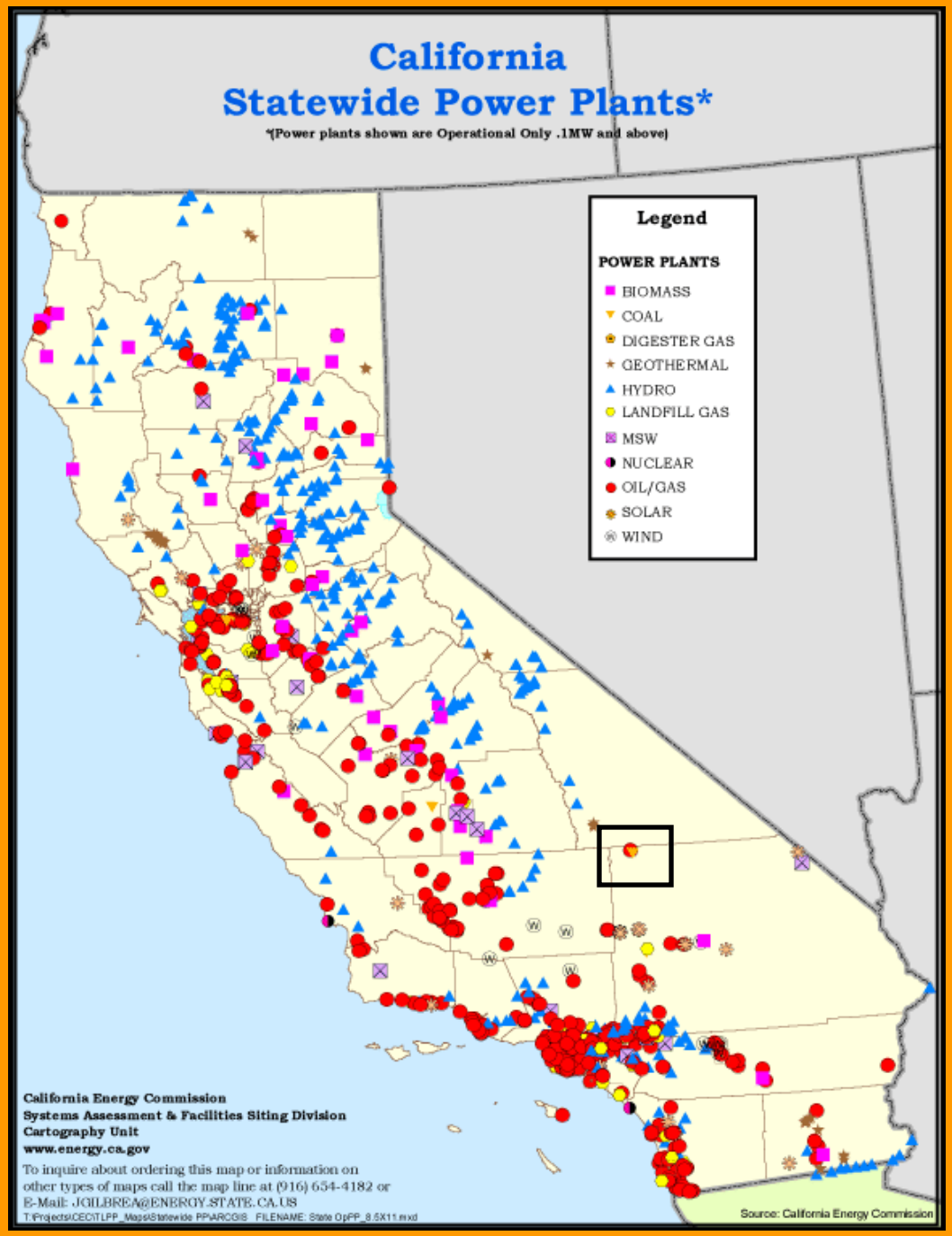
$\longrightarrow$ .5 x .3 x .7 x 33 Tg yr^{-1} = **3.5 Tg yr^{-1}**

- Note β-pinene ~10% of total terpene emissions
  ~ 33 Tg yr^{-1} SOA??

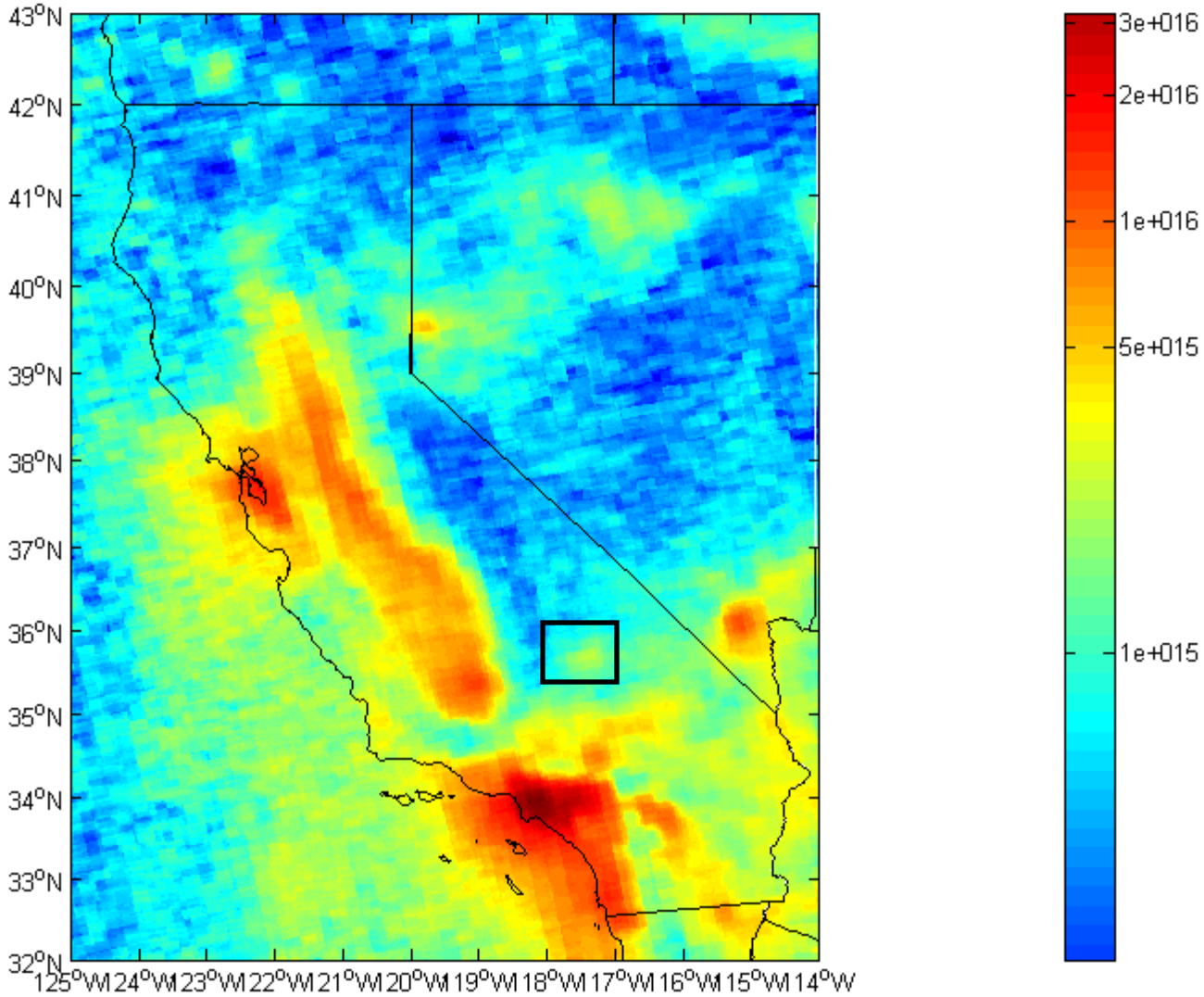
SOA source estimates:
Kanakidou et al, 2005: 12 – 70 Tg $year^{-1}$
Goldstein & Galbally, 2007: 140 – 910 Tg $year^{-1}$

Emissions

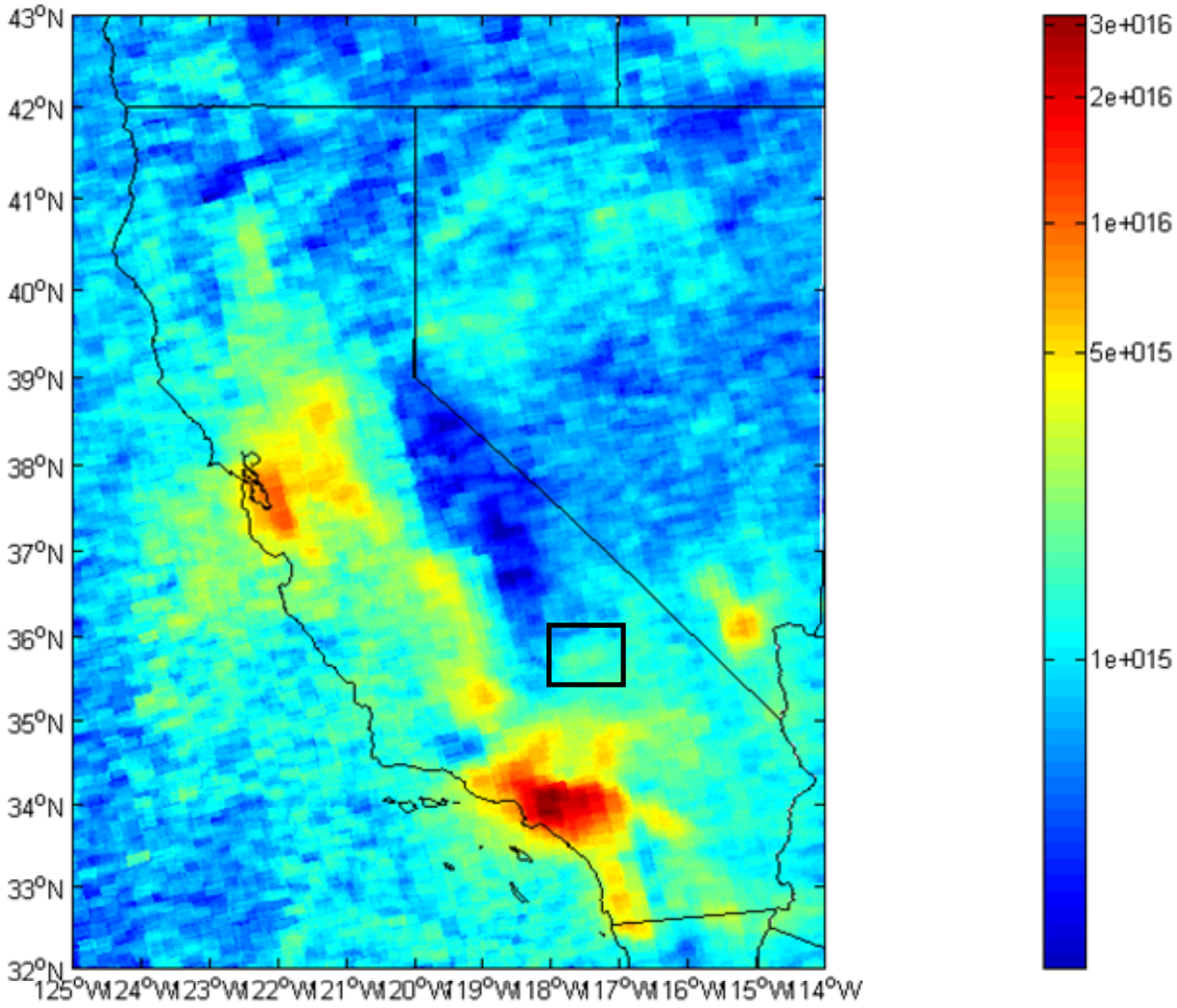
- Satellite observations are on track to be the best information about emissions.
- Now 3 instruments: 9:30, 10:30 and 1:30 13x24km to 40x60km pixels.
- In planning phase, GEO-CAPE continuous daytime monitoring ~5km pixels


California
Statewide Power Plants*
*(Power plants shown are Operational Only .1MW and above)
Legend
POWER PLANTS
BIOMASS
COAL
DIGESTER GAS
GEOTHERMAL
HYDRO
LANDFILL GAS
MSW
NUCLEAR
OIL/GAS
SOLAR
WIND
California Energy Commission
Systems Assessment & Facilities Siting Division
Cartography Unit
www.energy.ca.gov
To inquire about ordering this map or information on
other types of maps call the map line at (916) 654-4182 or
E-Mail: JGILBREA@ENERGY.STATE.CA.US
T:\Projects\CEC\TLPP_Maps\Statewide PP\ARCGIS FILENAME: State OpPP_8.5X11.mxd
Source: California Energy Commission

December 2006



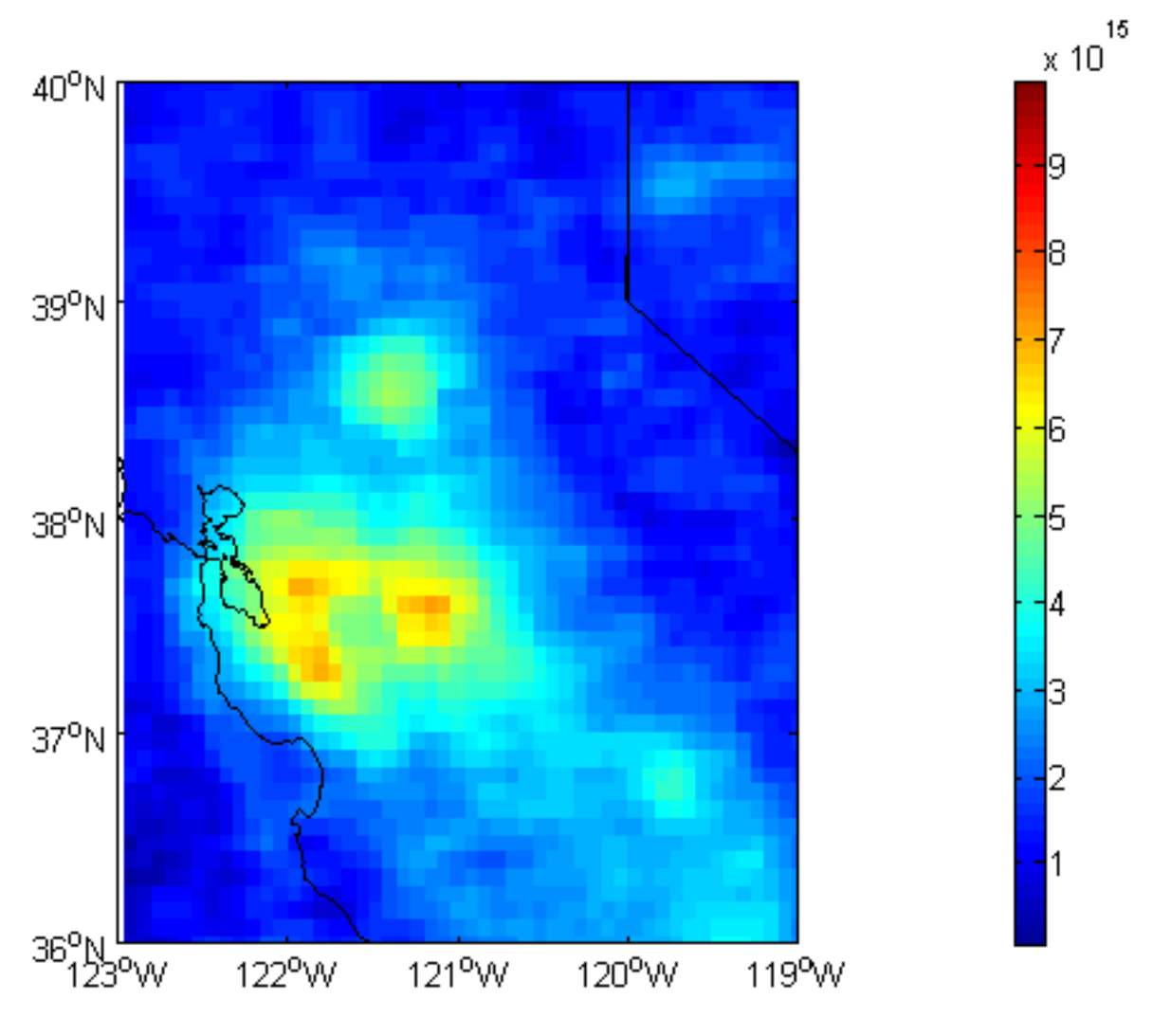
April 2006


43°N
42°N
41°N
40°N
39°N
38°N
37°N
36°N
35°N
34°N
33°N
32°N
125°W 124°W 123°W 122°W 121°W 120°W 119°W 118°W 117°W 116°W 115°W 114°W
3e+016
2e+016
1e+016
5e+015
1e+015

Satellite observations of NO_2 are much more accurate than the ground based network which has a bias of as much as 300% that varies in space, in time on diurnal and seasonal scales and is not independent of instrument configuration.

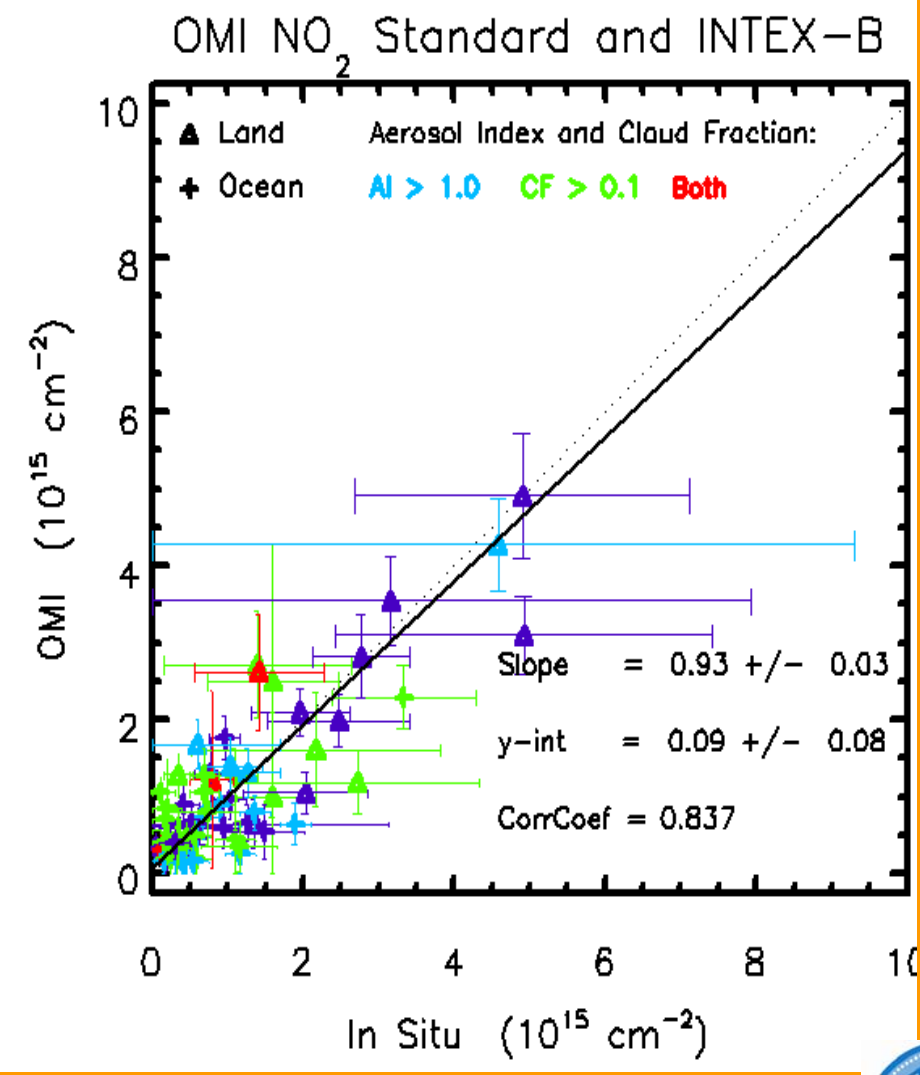
Satellite observations are not biased by local proximity to highways, etc.

Resolution: 0.04° x 0.04° (~ 4km x 4km)



Data from July 2006

NO_2 Satellite Comparison



See in press papers by

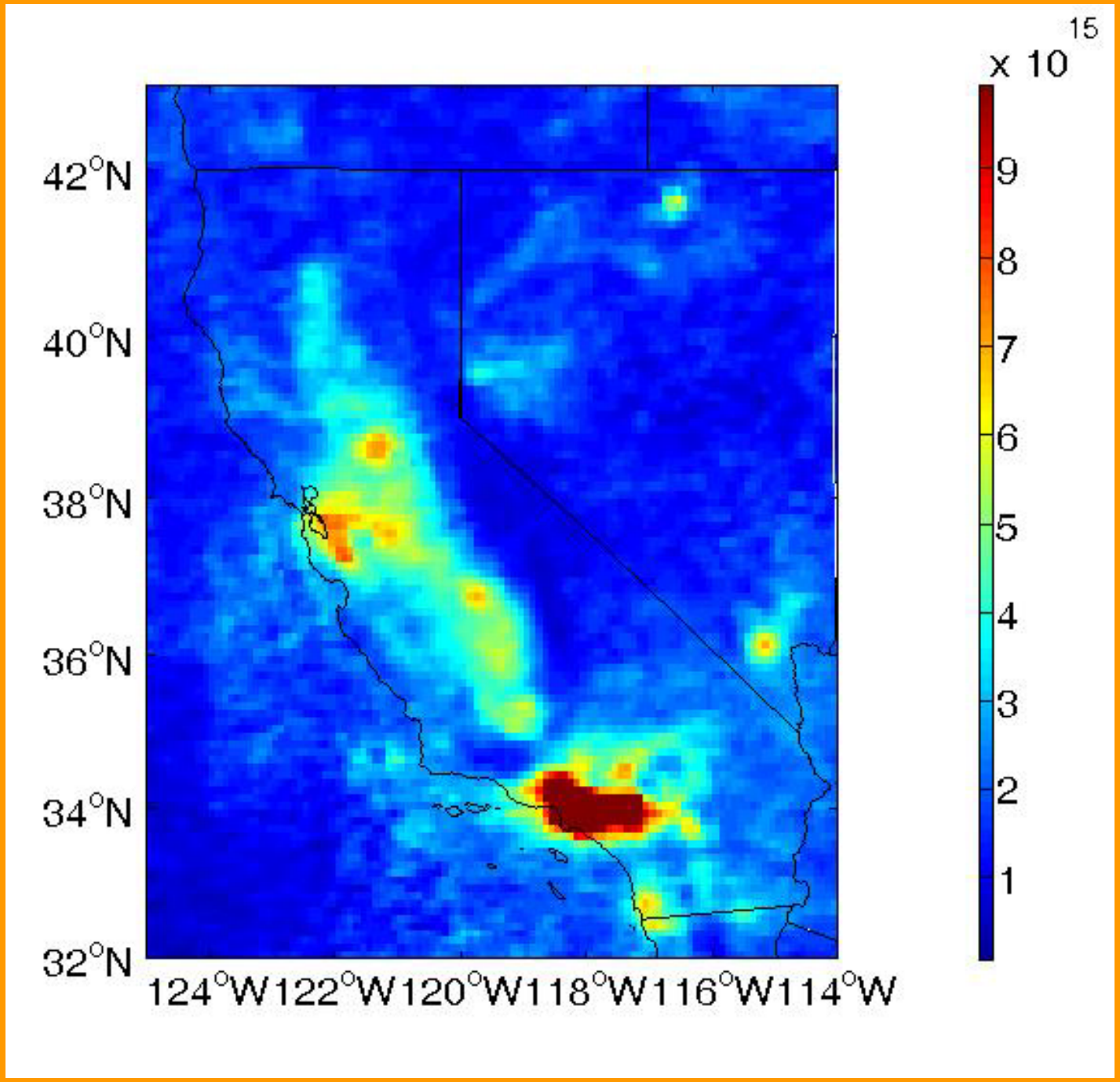
Bucsela et al. JGR
Boersma et al. Atm. Env.

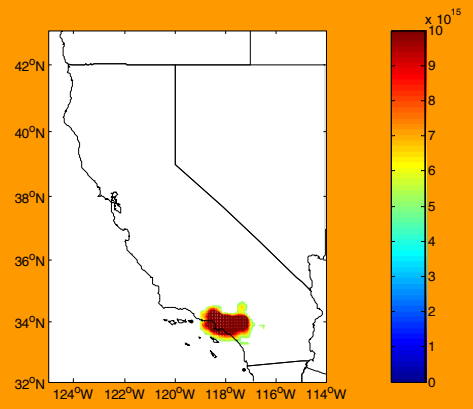
OMI

1:30 PM

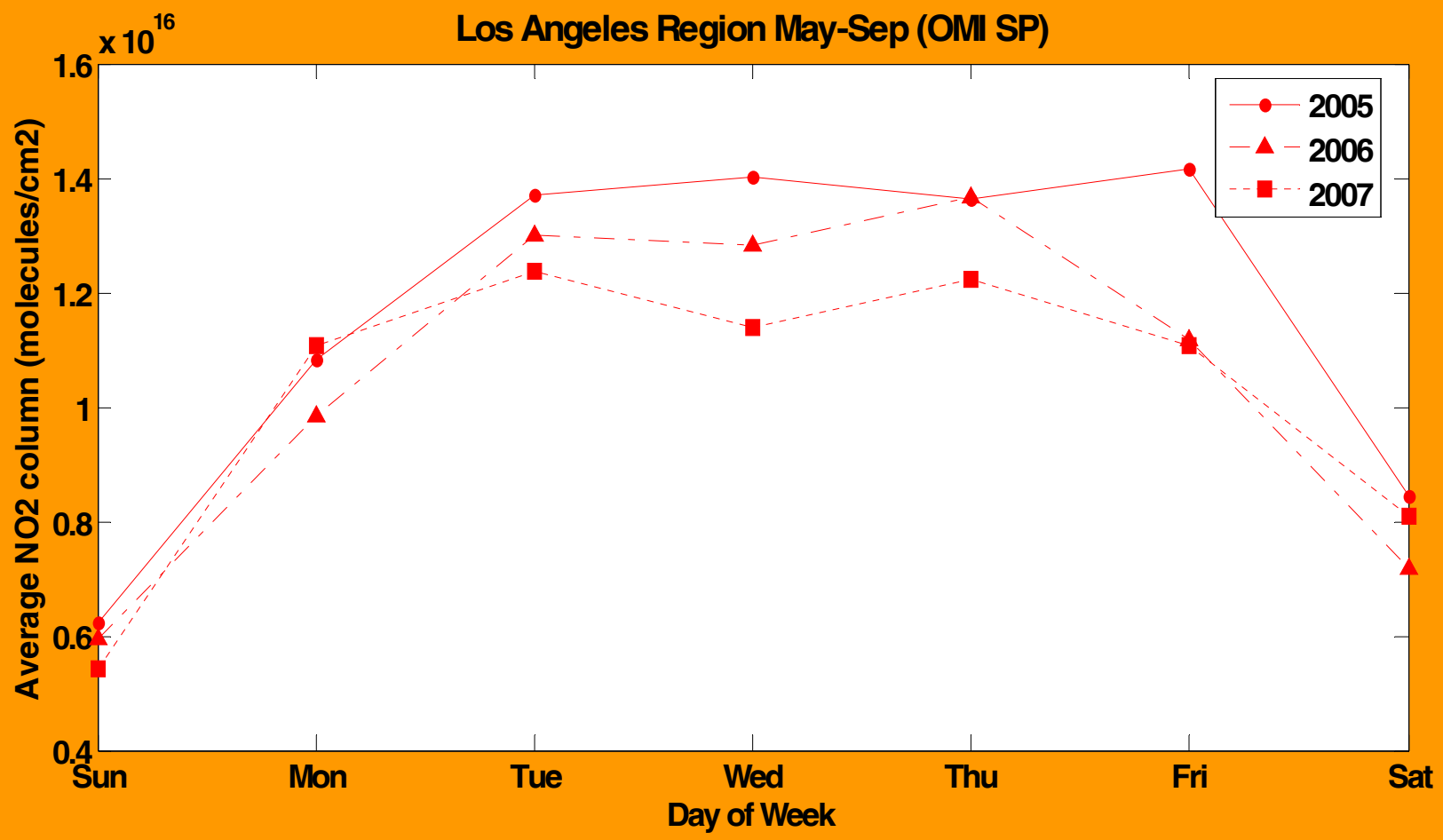
JULY 2006

4x4km



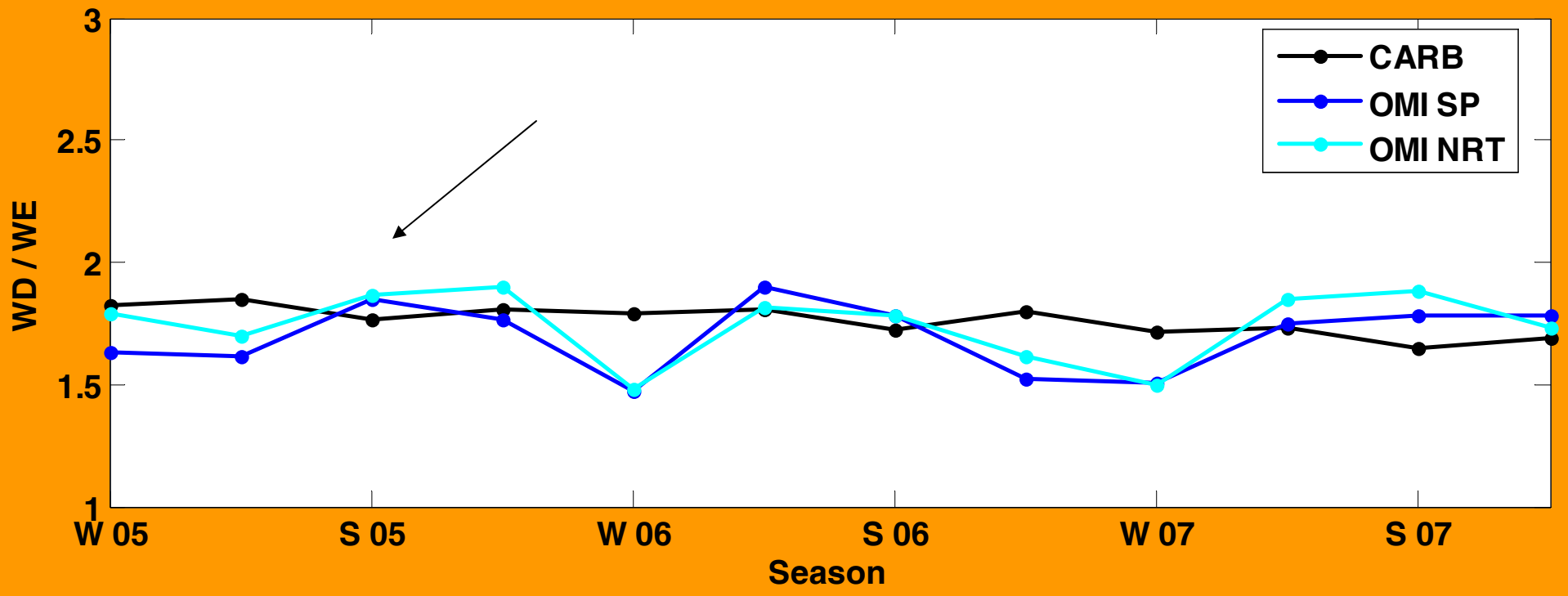

42°N
40°N
38°N
36°N
34°N
32°N
124°W 122°W 120°W 118°W 116°W 114°W
x 10^15
10
9
8
7
6
5
4
3
2
1
0

Trends


Los Angeles Region May-Sep (OMI SP)
x 10^16
1.6
1.4
1.2
1
0.8
0.6
0.4
Average NO2 column (molecules/cm2)
Sun
Mon
Tue
Wed
Thu
Fri
Sat
Day of Week
2005
2006
2007

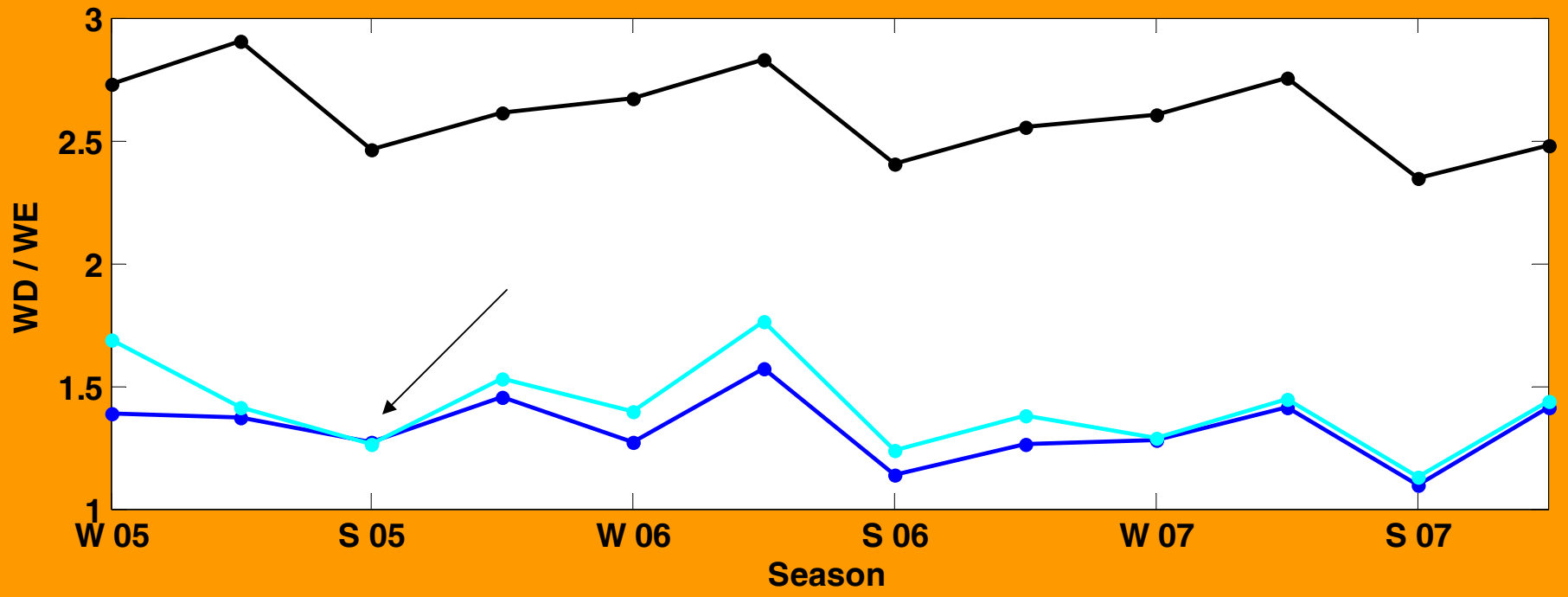
Weekday/Weekend NO_2:

Closest approximation to measure of emissions in summer, when there is the smallest memory of the previous day.



South Coast Air Basin

San Joaquin Valley Air Basin



Conclusions:

Observations demonstrate that chemistry will run faster in a warmer climate than in our models.

If this is the only significant error (and it is not) this means the atmosphere is closer to being NO_x limited than we are predicting and that NO_x controls will be more effective than we are predicting.

$RONO_2$ formation/lifetimes in some models are too high/long

This changes the sign of model response to increasing T, where biogenics are dominant.

NO_3 + biogenics have high SOA yields

More SOA in a warmer climate?

Satellites are on the cusp of providing NO_x emission inventories and are already a strong constraint on models.

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Jennifer Murphy	PhD	’05
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Patricia Cleary	PhD	’03
Michael Dillon	PhD	‘02
Joel Thornton	PhD	’02
Melissa Hendricks	PhD	‘00

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Cohen Group
Thank you