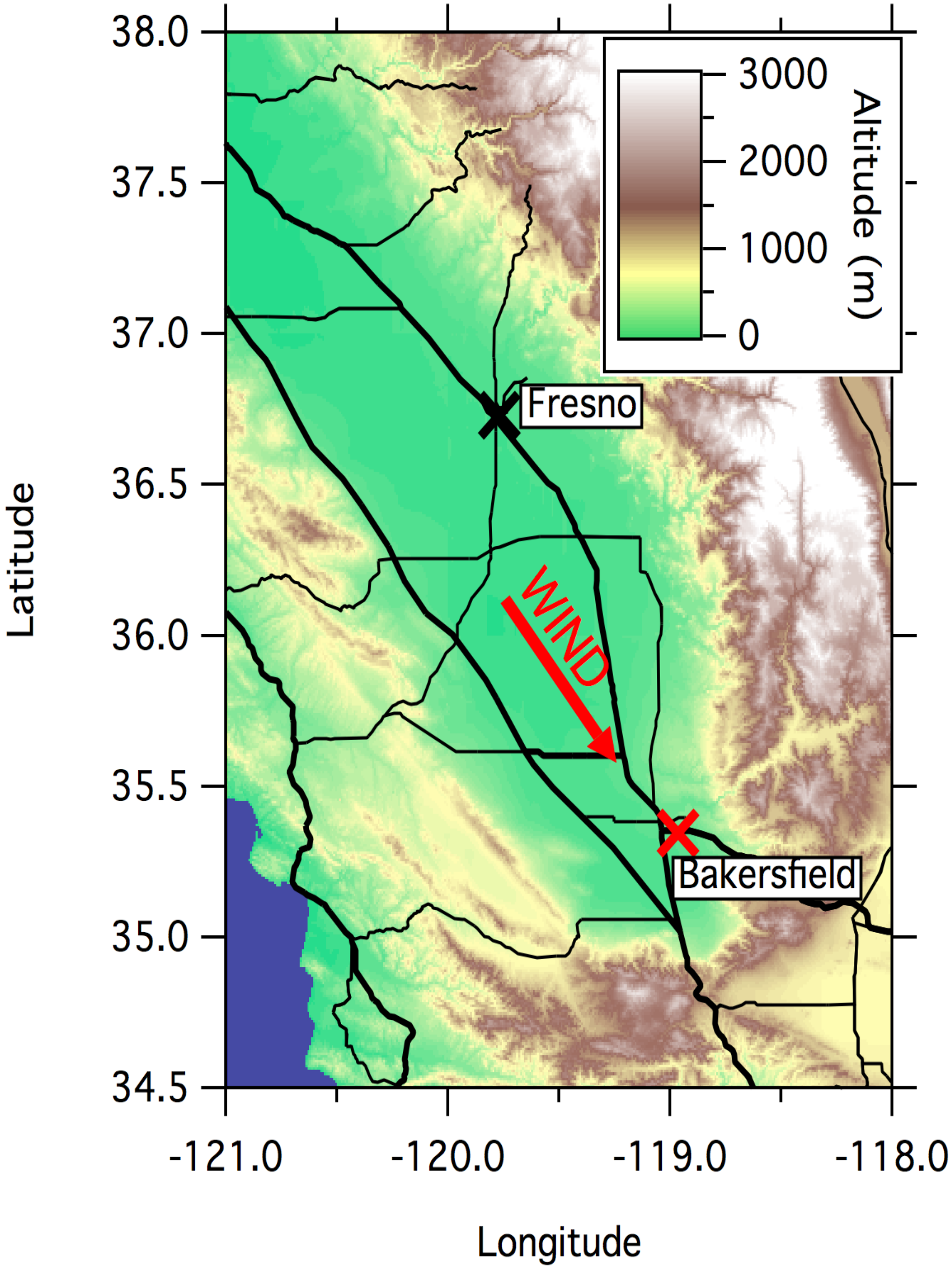
SJV Air Quality: Insights from CALNEX 2010

Ronald C. Cohen
CALNEX-SJV Team
April 2013



38.0
37.5
37.0
36.5
36.0
35.5
35.0
34.5
Latitude
-121.0
-120.0
-119.0
-118.0
Longitude
3000
2000
1000
0
Altitude (m)
Fresno
WIND
Bakersfield

Research Teams:

This ARB Contract:

Measurements and Analysis
Cohen & Goldstein

Measurements Only
Keutsch, Thornton, Wennberg, Brune

Other ARB Contracts

Goldstein, Russell

Other Financial Support

Murphy, Ren, Surratt, Zondlo

Measurements

Meteorology and slowly reacting tracers/GHGs

wind, T, RH, CO, CO_2, N_2O, CH_4

Nitrogen radical chemistry

NO, NO_2, HONO, ΣRO_2NO_2, $\Sigma RONO_2$, PAN, PPN, HNO_3, Aerosol phase organic nitrates (ΣANs_{aer}), NO_3^-, NO_2^-, NH_3, HCN, + ...

Hydrogen radical chemistry

OH, HO_2, H_2CO, CHOCHO, H_2O_2, CH_3COOH, HCOOH, OH reactivity

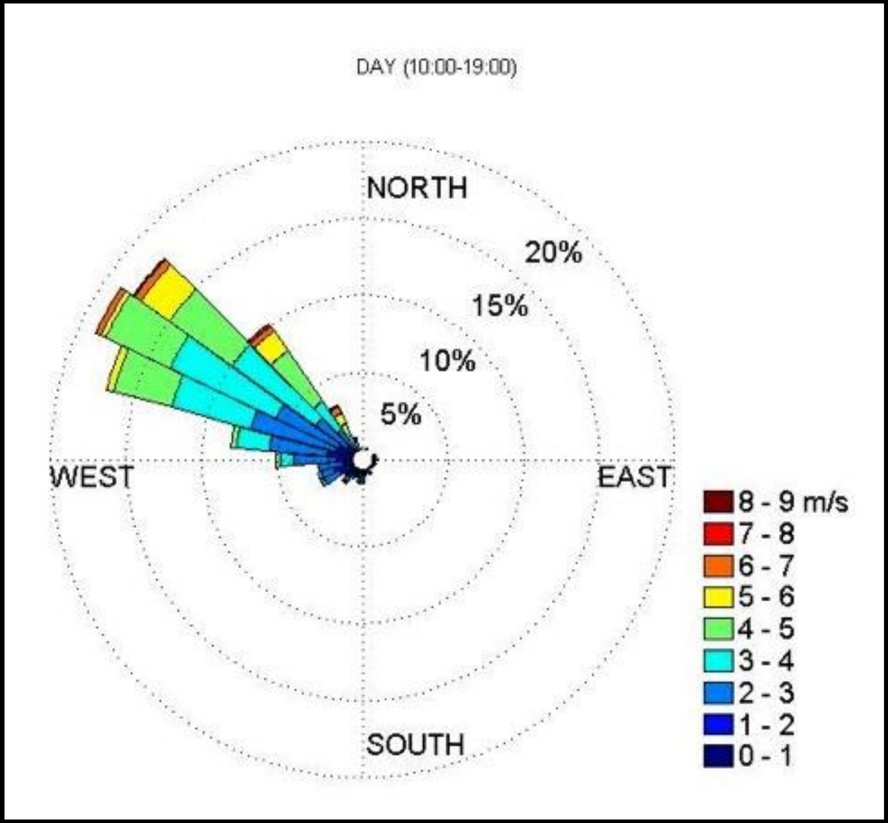
Organic chemistry of gases and aerosol

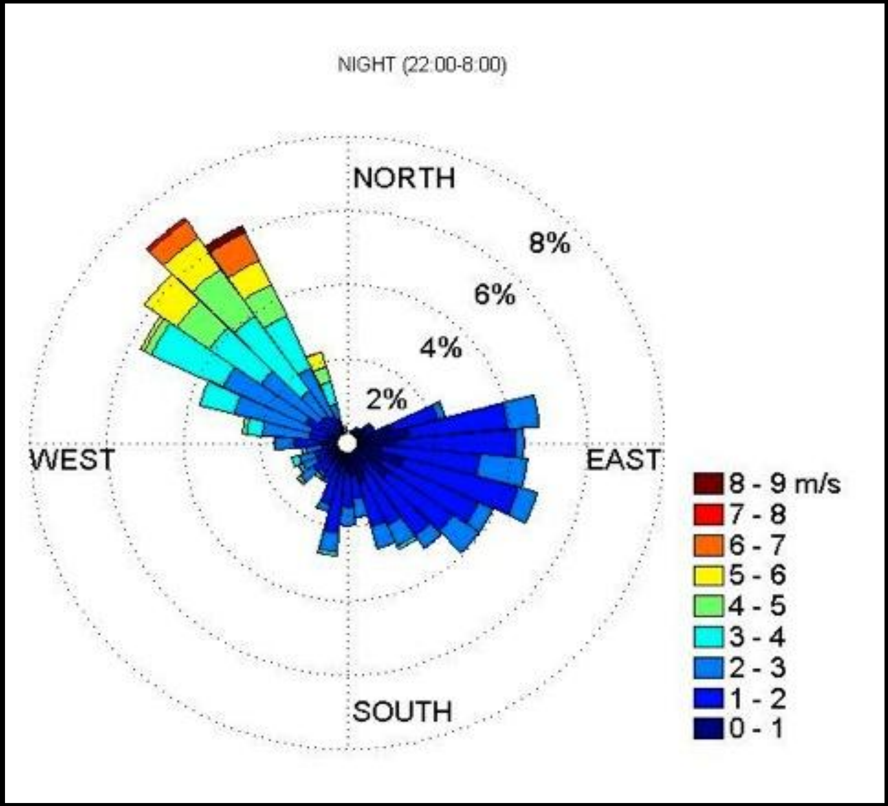
many, many VOCs (see Goldstein talk),

Aerosol inorganic chemistry

HCl, aerosol inorganic ions, aerosol composition, aerosol physical properties

Winds

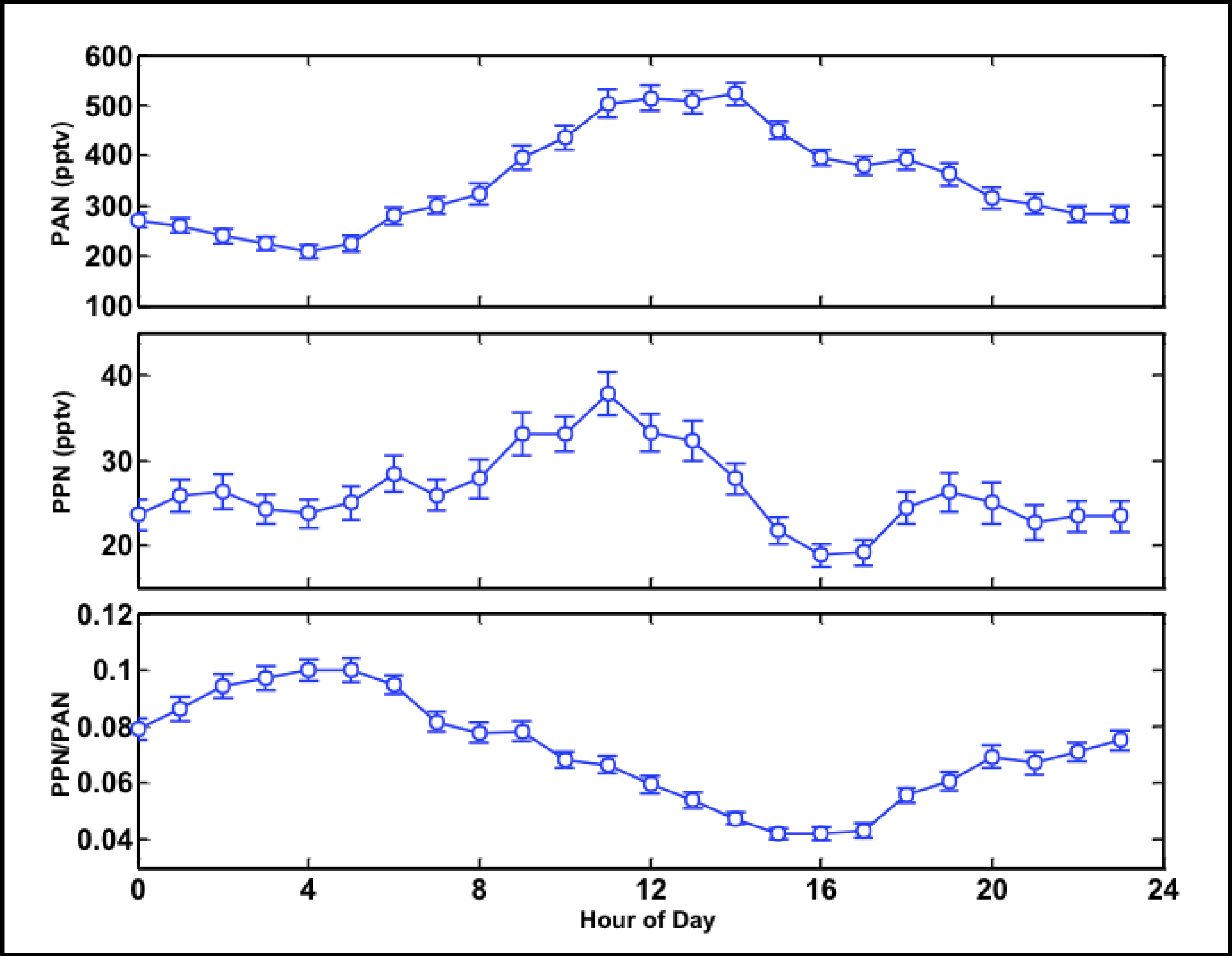




Day

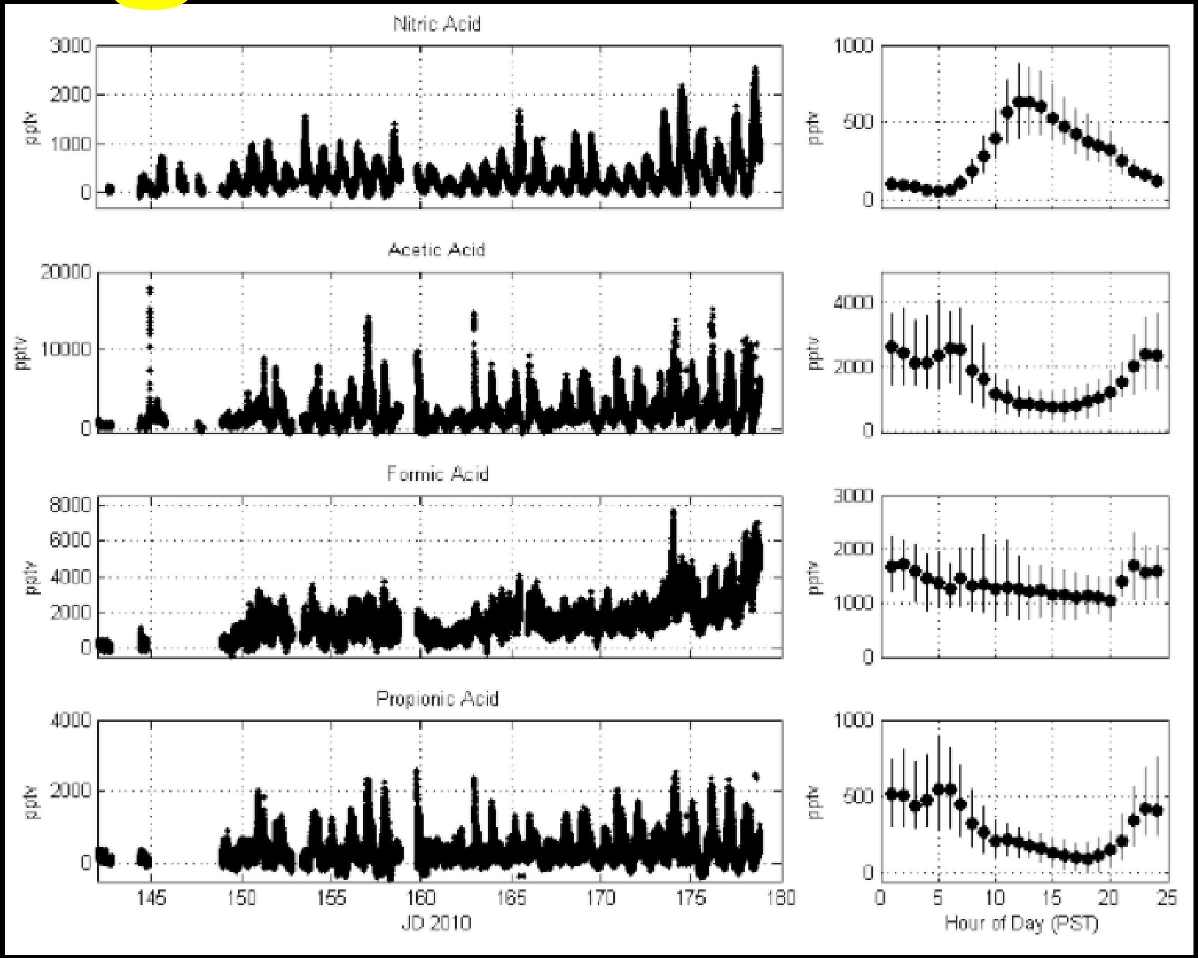
Night

PAN and PPN



Thornton et al. Univ of Washington, Seattle

Inorganic and Organic Acids



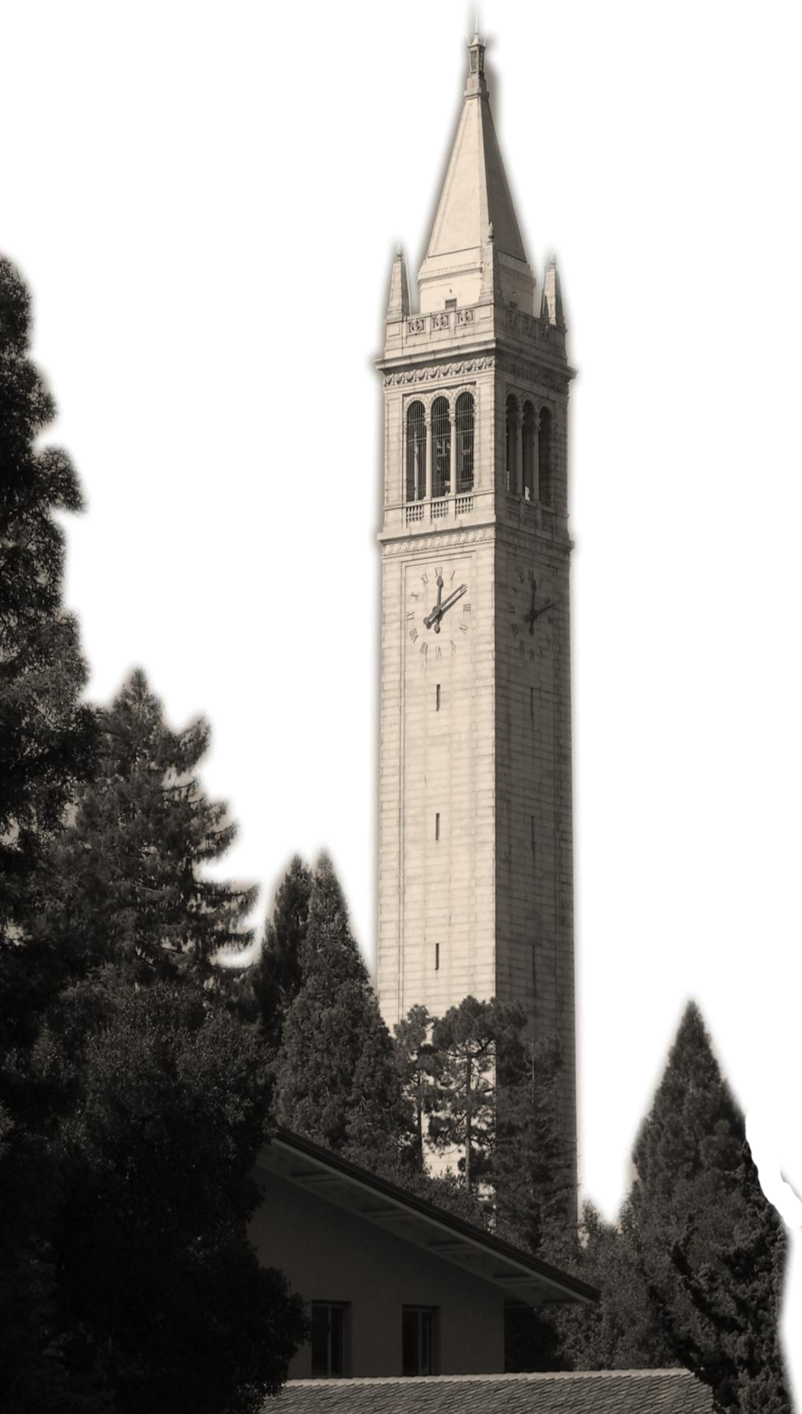
HNO_3

CH_3COOH

$HCOOH$

C_2H_5COOH

Wennberg et al. Caltech

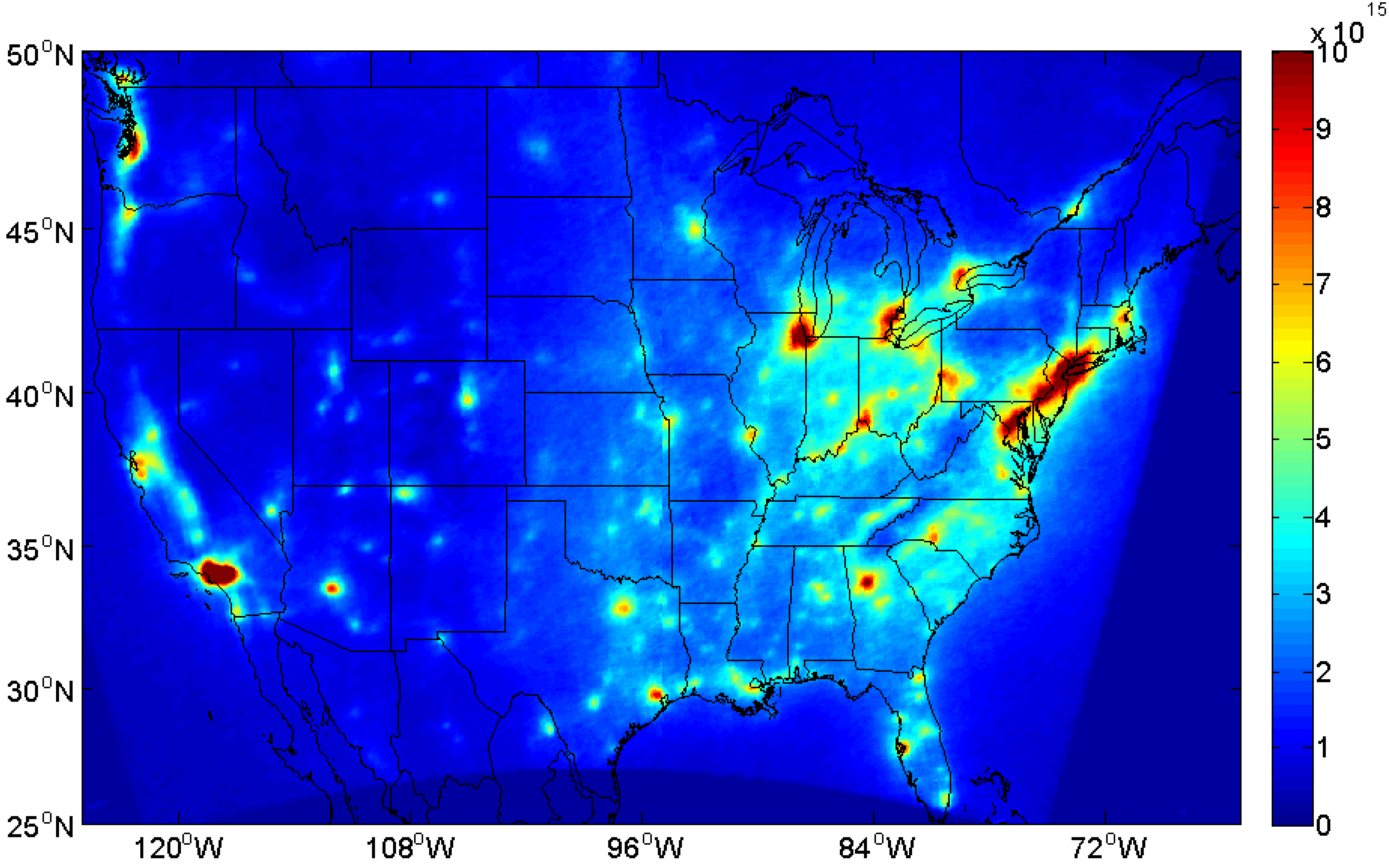


Overview

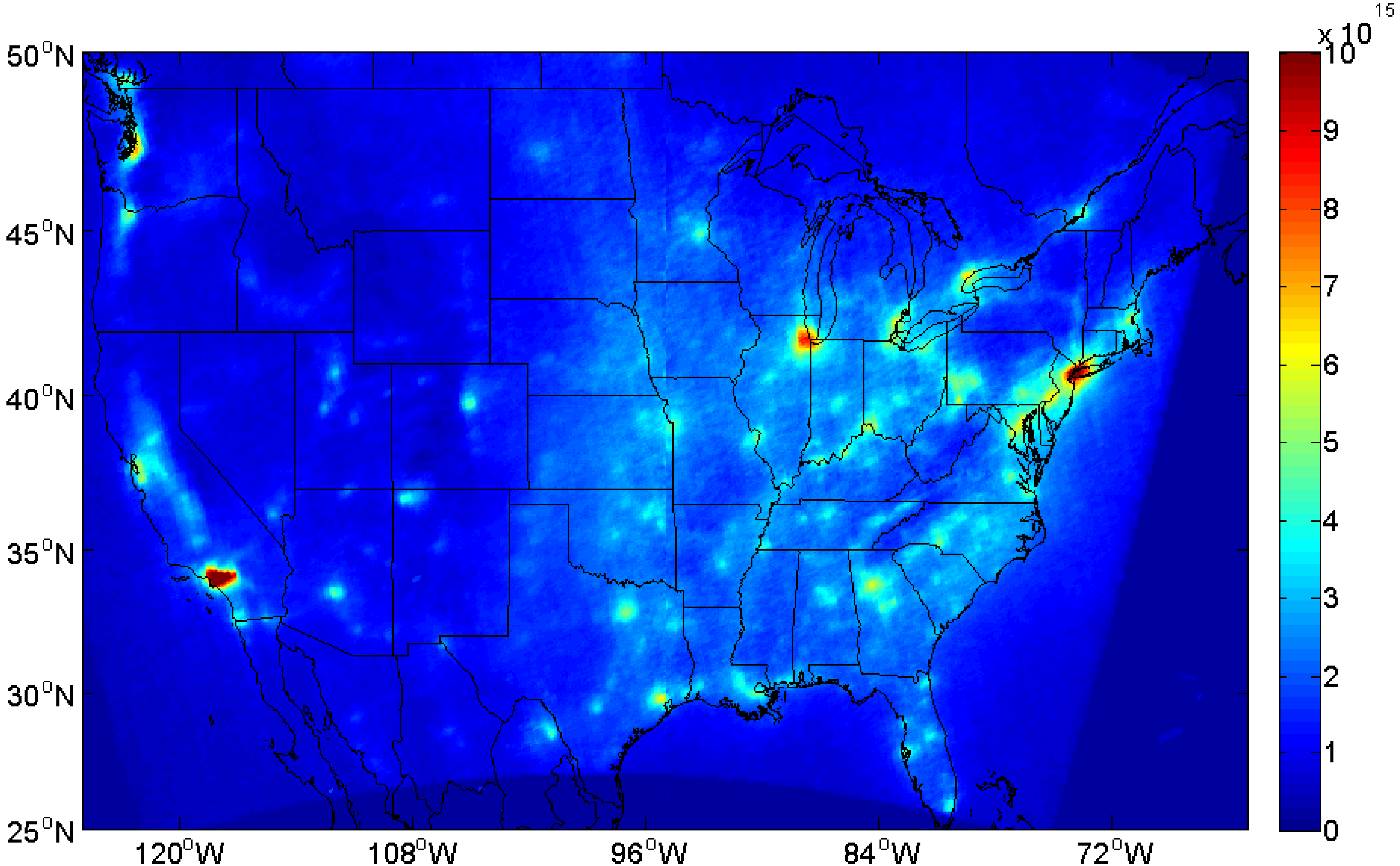
O_3 trends vs. NO_x and VOC Controls

$RONO_2$ content of aerosol


LGR

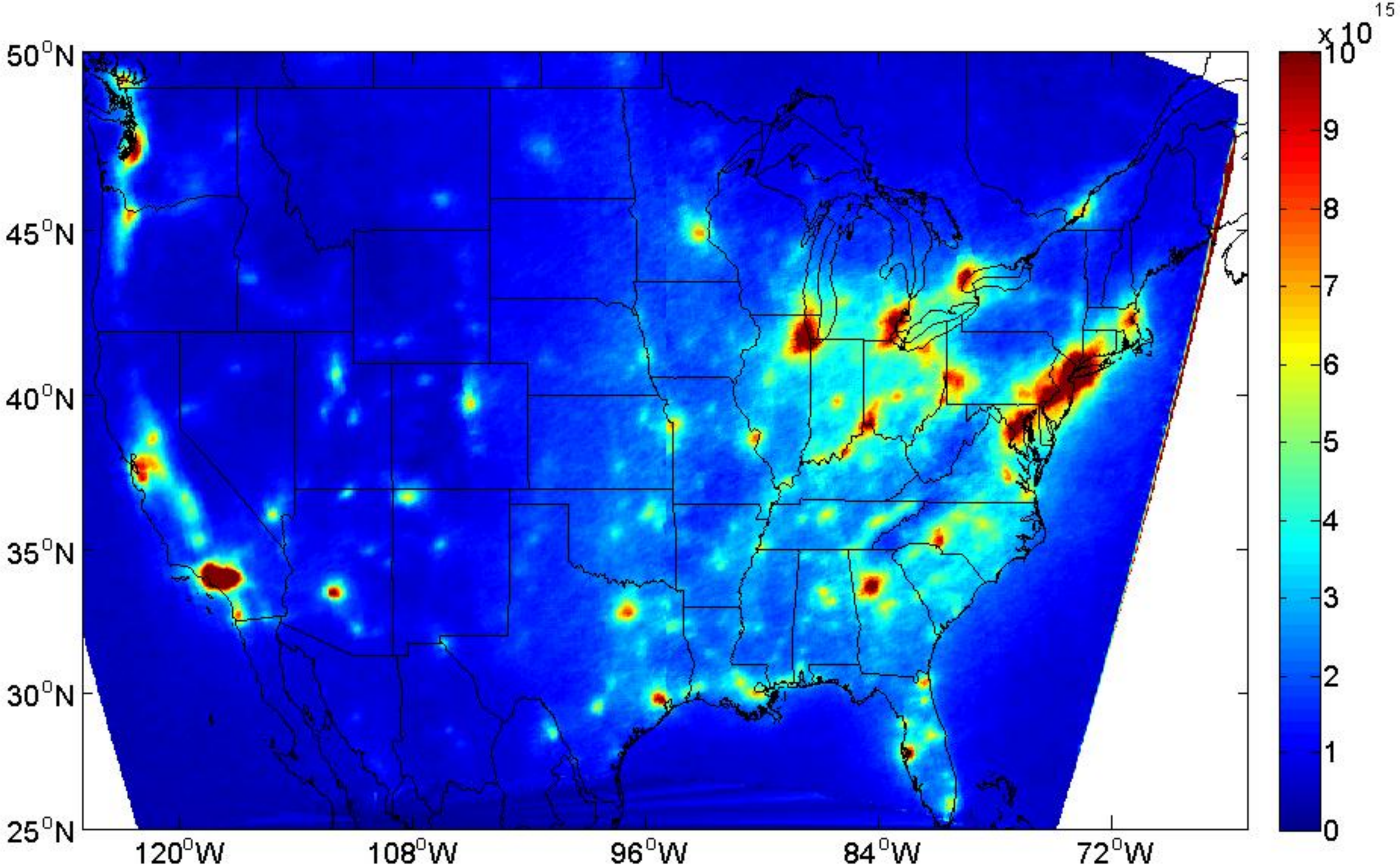

50°N
45°N
40°N
35°N
30°N
25°N
120°W
108°W
96°W
84°W
72°W
x 10^15
10
9
8
7
6
5
4
3
2
1
0

Summer 2005

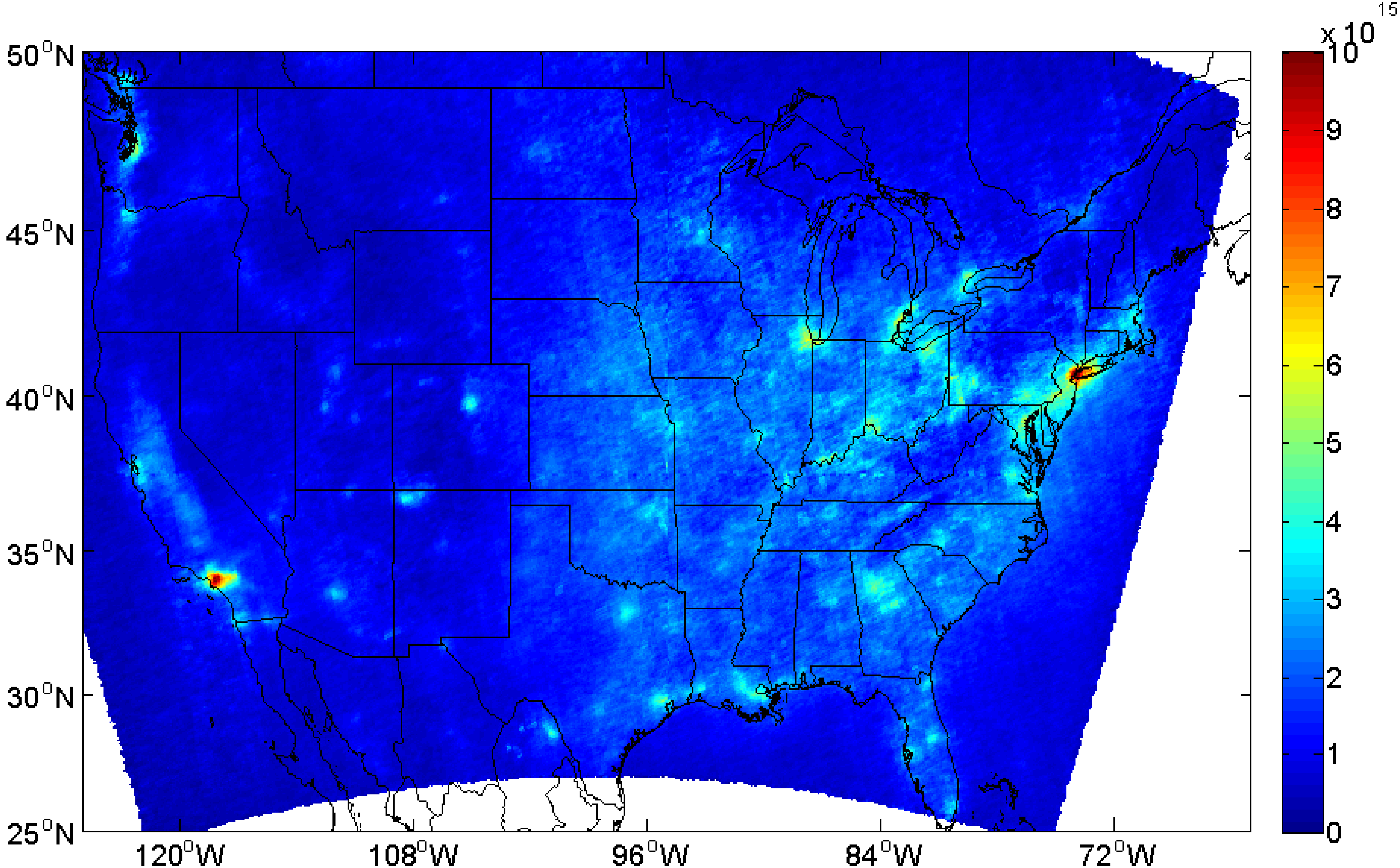


50°N
45°N
40°N
35°N
30°N
25°N
120°W
108°W
96°W
84°W
72°W
x 10^15
10
9
8
7
6
5
4
3
2
1
0

Summer 2011

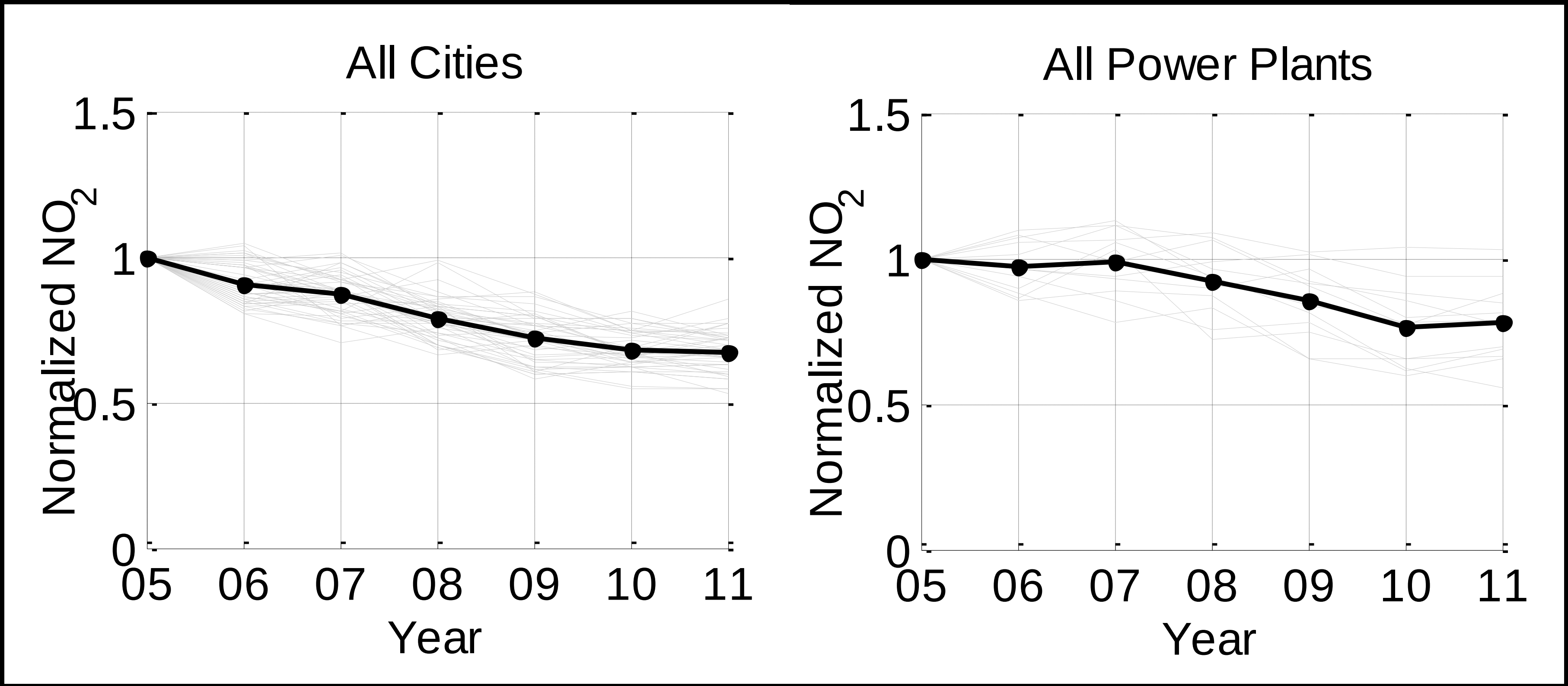


Weekday 2005



Weekend 2011

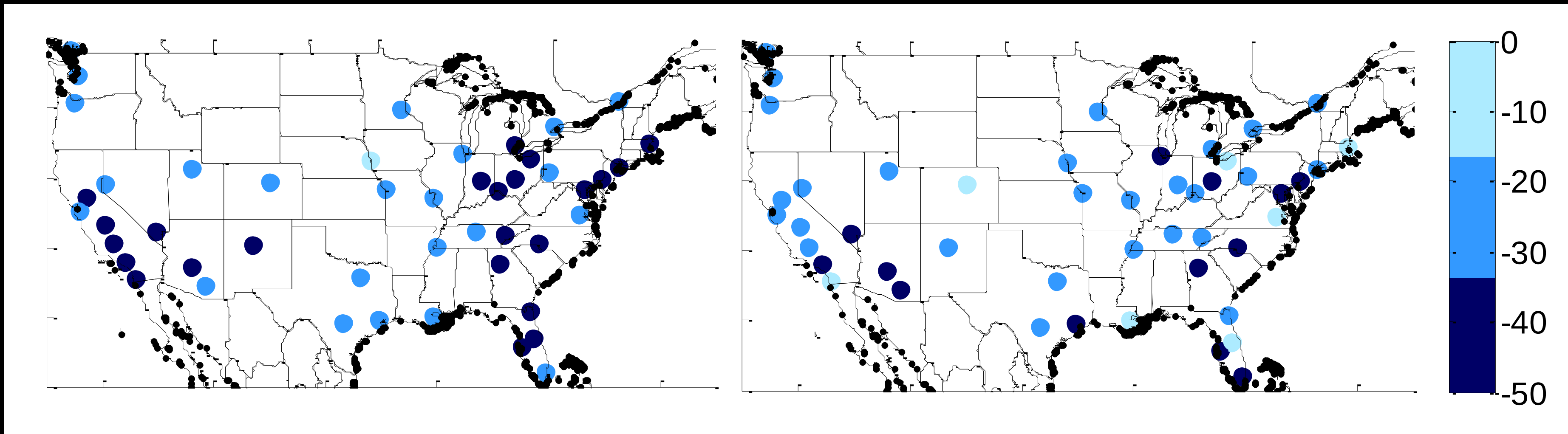
Trends in cities are similar while trends at power plants are more variable



47 cities, 23 power plants!

Russell et al., ACPD 2012

Reductions on weekdays are larger than those on weekends due to reductions in diesel traffic and/or diesel emissions



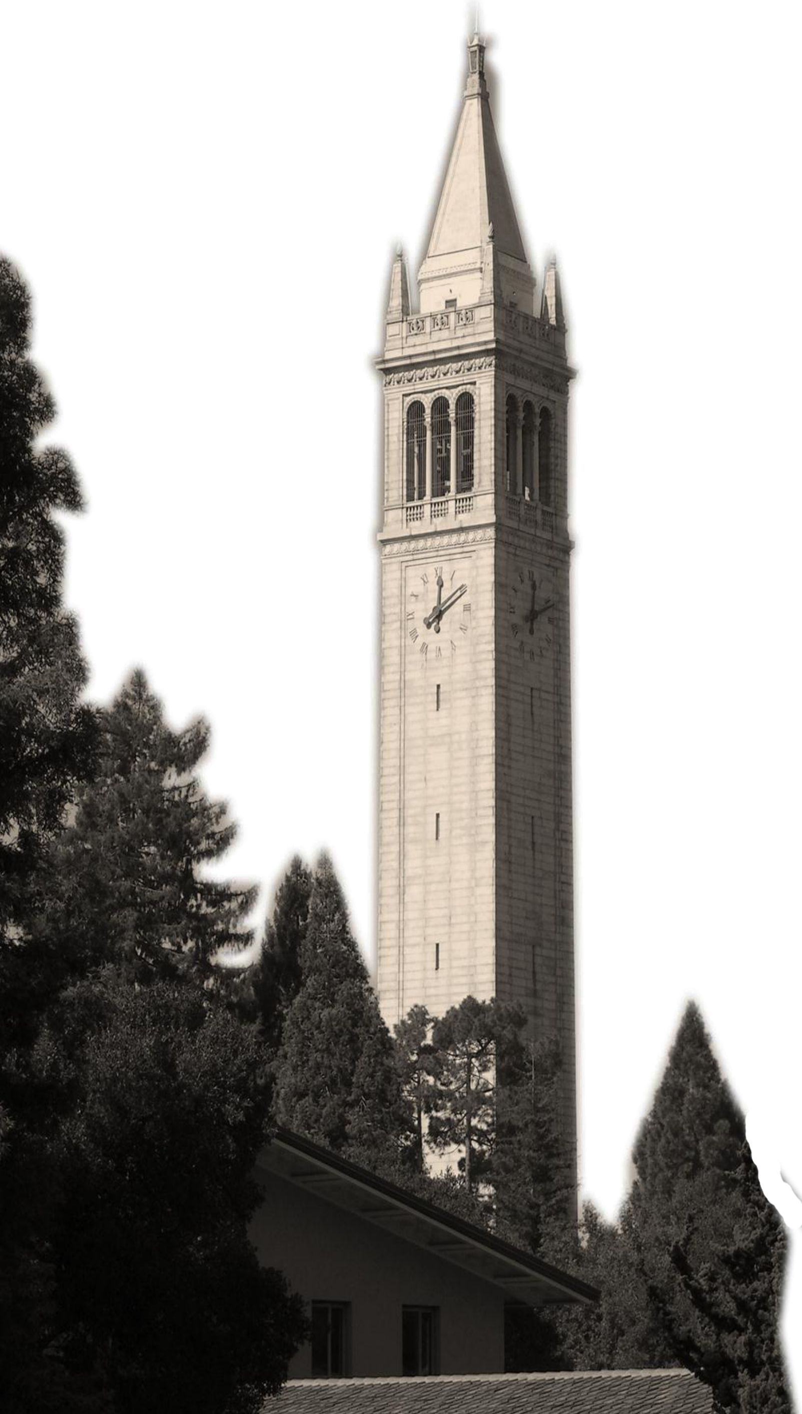
Weekdays: –34 ± 8%

Weekends: –27 ± 10%

	2005 – 2007	2007 – 2009	2009 – 2011
Weekday	– 6 ± 4%	– 9 ± 4%	– 4 ± 4%
Weekend	– 7 ± 5%	– 6 ± 7%	– 1 ± 7%

Russell et al., ACPD 2012

How do these trends affect O_3 and aerosol?



Overview

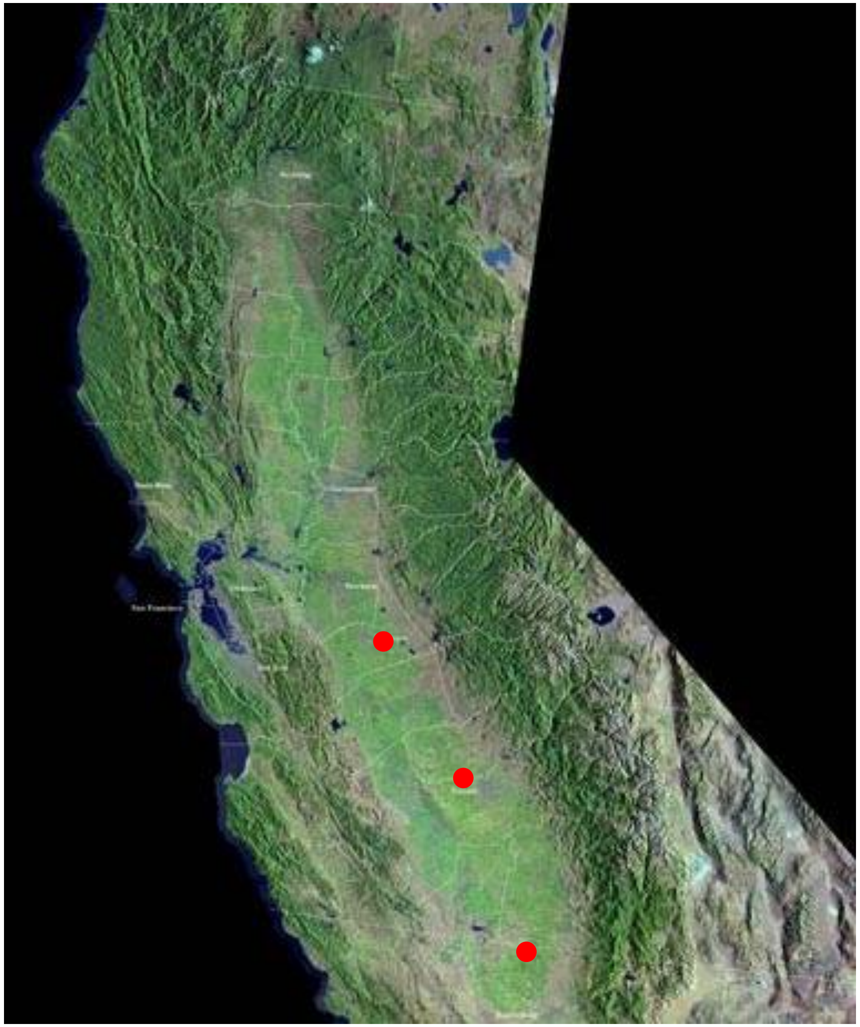
O_3 trends vs. NO_x and VOC Controls

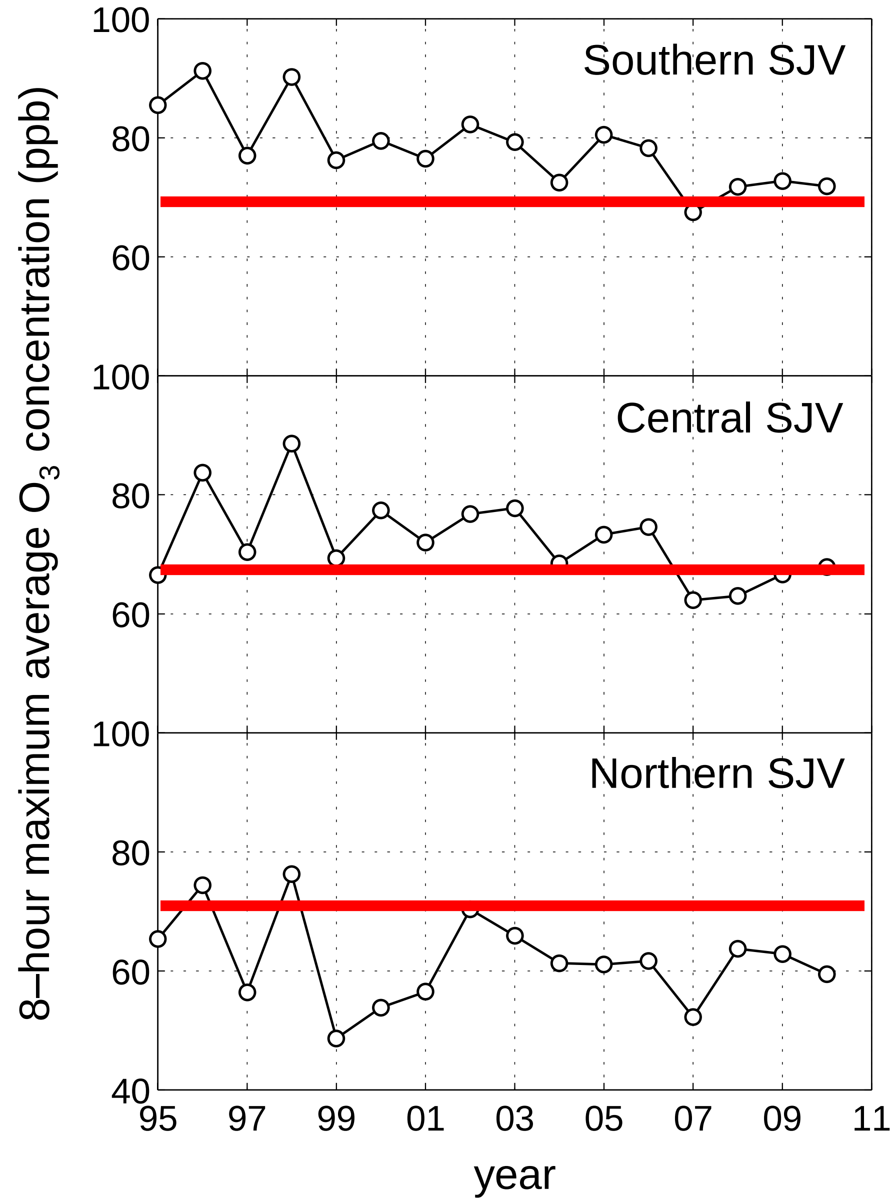
$RONO_2$ content of aerosol

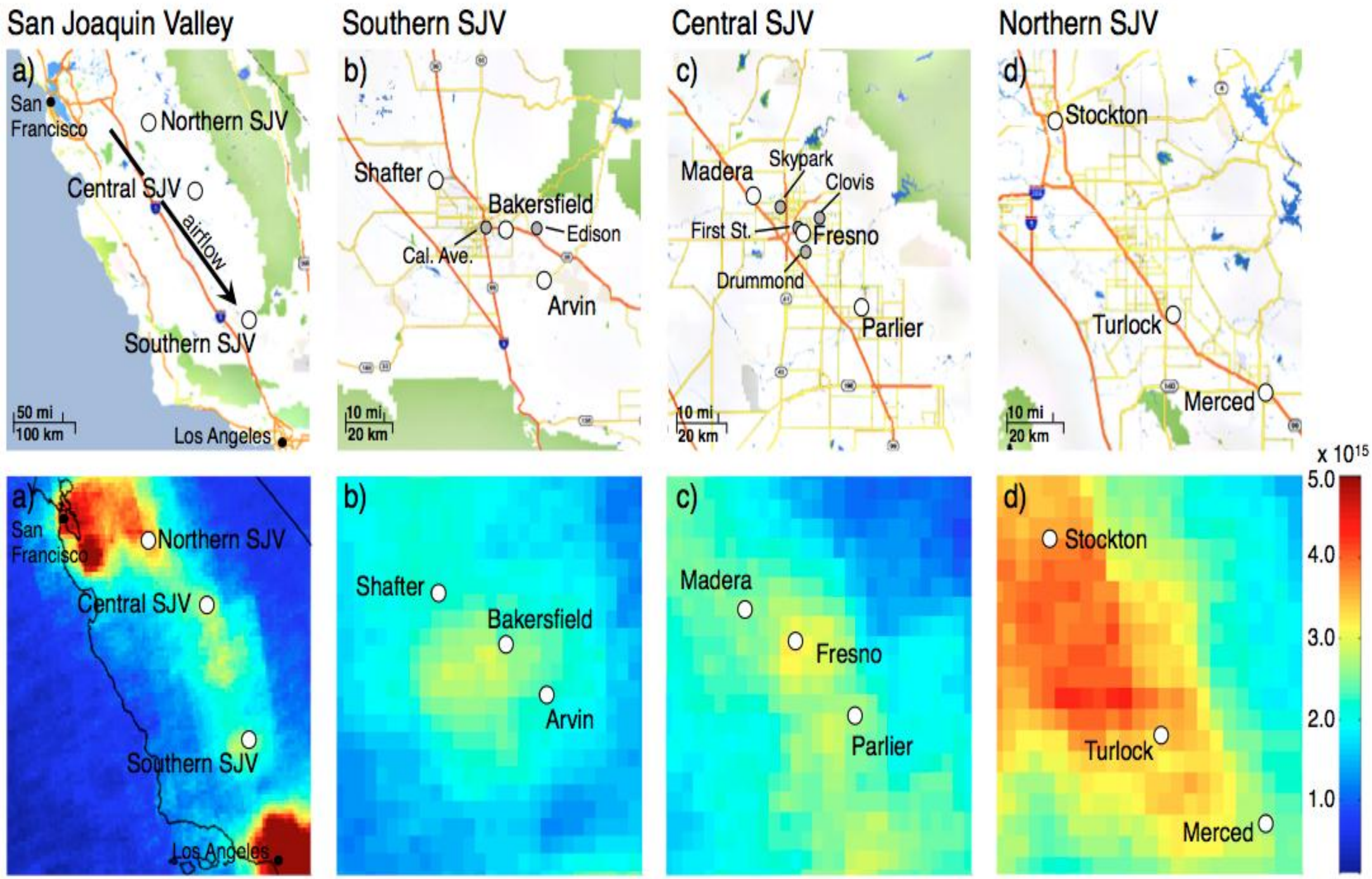
Sally Pusede

Pusede and Cohen ACP 2012

Ozone Medians (8hr, June-August) 1995–2010






San Joaquin Valley
Southern SJV
Central SJV
Northern SJV
a)
San Francisco
Northern SJV
Central SJV
airflow
Southern SJV
50 mi
100 km
Los Angeles
b)
Shafter
Bakersfield
Edison
Cal. Ave.
Arvin
10 mi
20 km
c)
Madera
Skypark
Clovis
First St.
Fresno
Drummond
Parlier
10 mi
20 km
d)
Stockton
Turlock
Merced
10 mi
20 km
a)
San Francisco
Northern SJV
Central SJV
Southern SJV
Los Angeles
b)
Shafter
Bakersfield
Arvin
c)
Madera
Fresno
Parlier
d)
Stockton
Turlock
Merced
x 10^15
5.0
4.0
3.0
2.0
1.0

Recipe for Surface Ozone:

O_3 ~ Chemical Production - Dilution

Over the last 20 yrs:

Held Constant

- Sunlight
- Stagnation/temperature

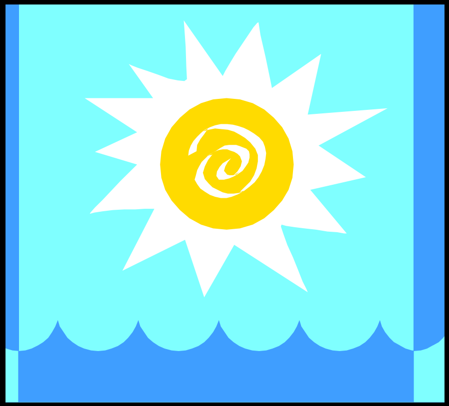
Not sure

- Organic molecules—yearly trends?
  - Not much day of week

Change

- Nitrogen oxides—day of week & trends

Initiated by sunlight (HO_x radicals)



$O_3 + h\nu \rightarrow O^1D$

$O^1D + H_2O \rightarrow 2OH$

>80%

$H_2CO + h\nu \rightarrow H + HCO$

$H, HCO + O_2 \rightarrow 2HO_2$

<20%

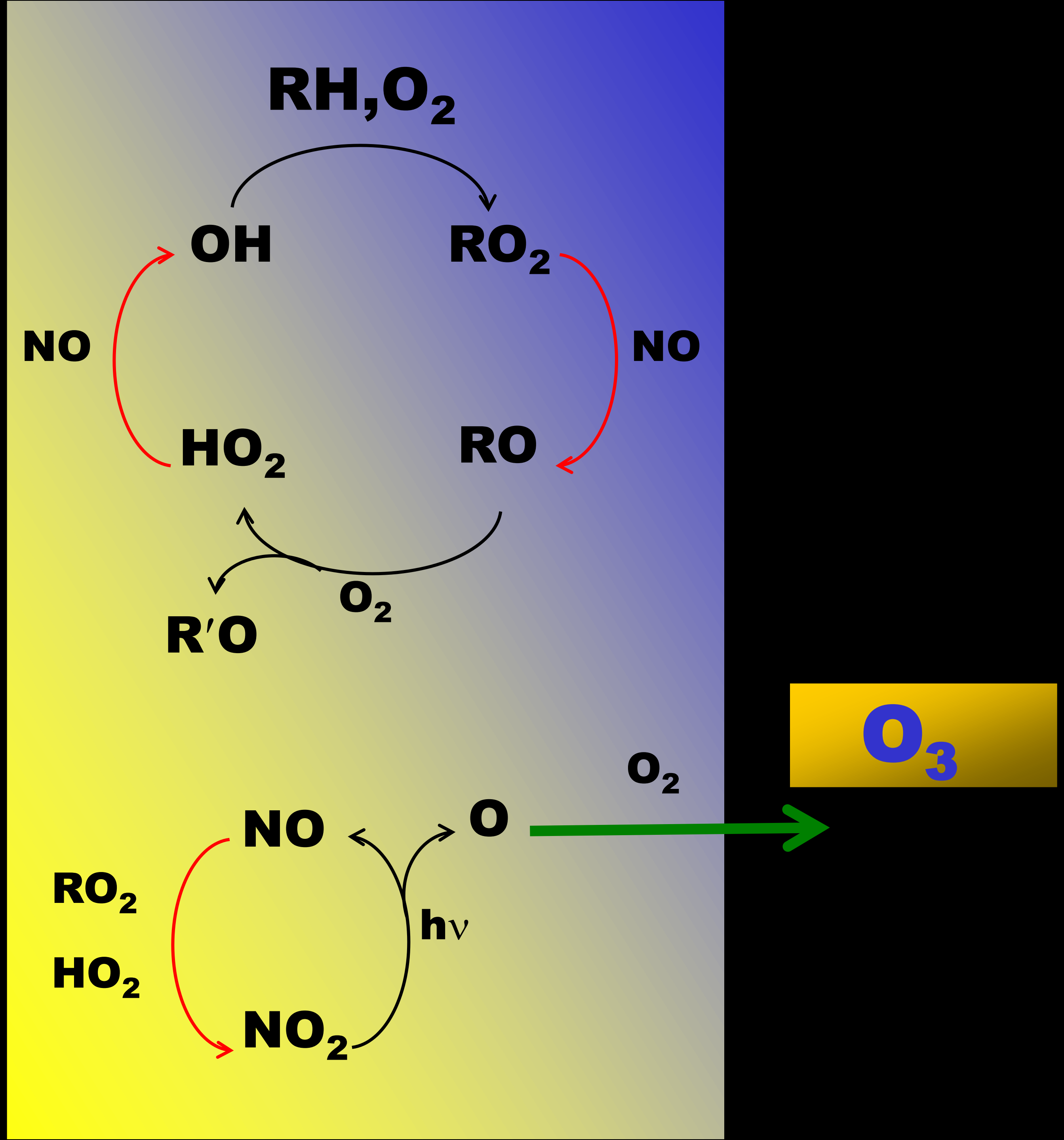
$HONO + h\nu \rightarrow OH + NO$

$ClNO_2 + h\nu \rightarrow Cl + NO$

Mostly at Sunrise

HO_x Cycle

NO_x Cycle



Chain Termination

HO_x- HO_x

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

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

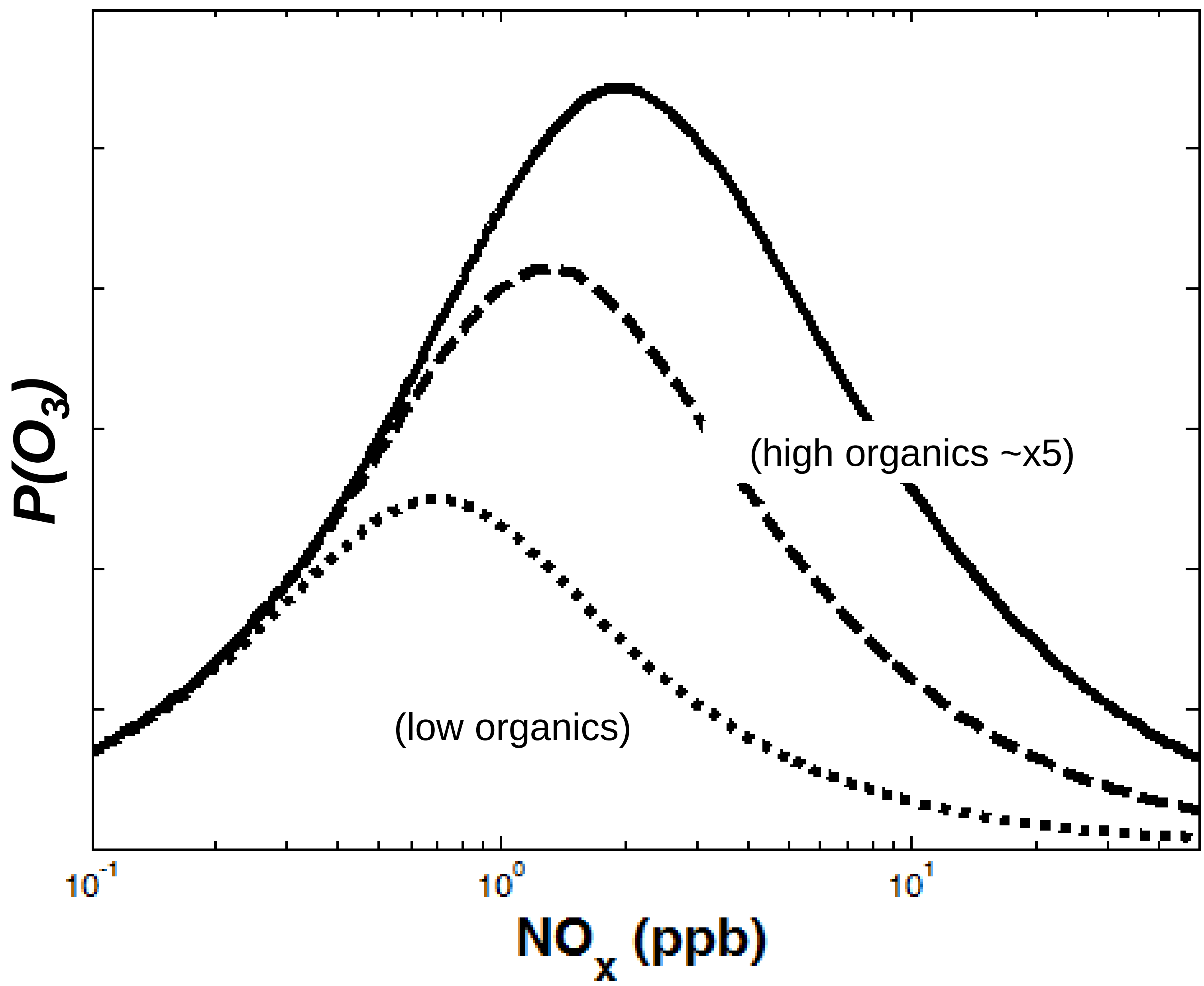
$$HO_2 + OH \longrightarrow H_2O + O_2$$

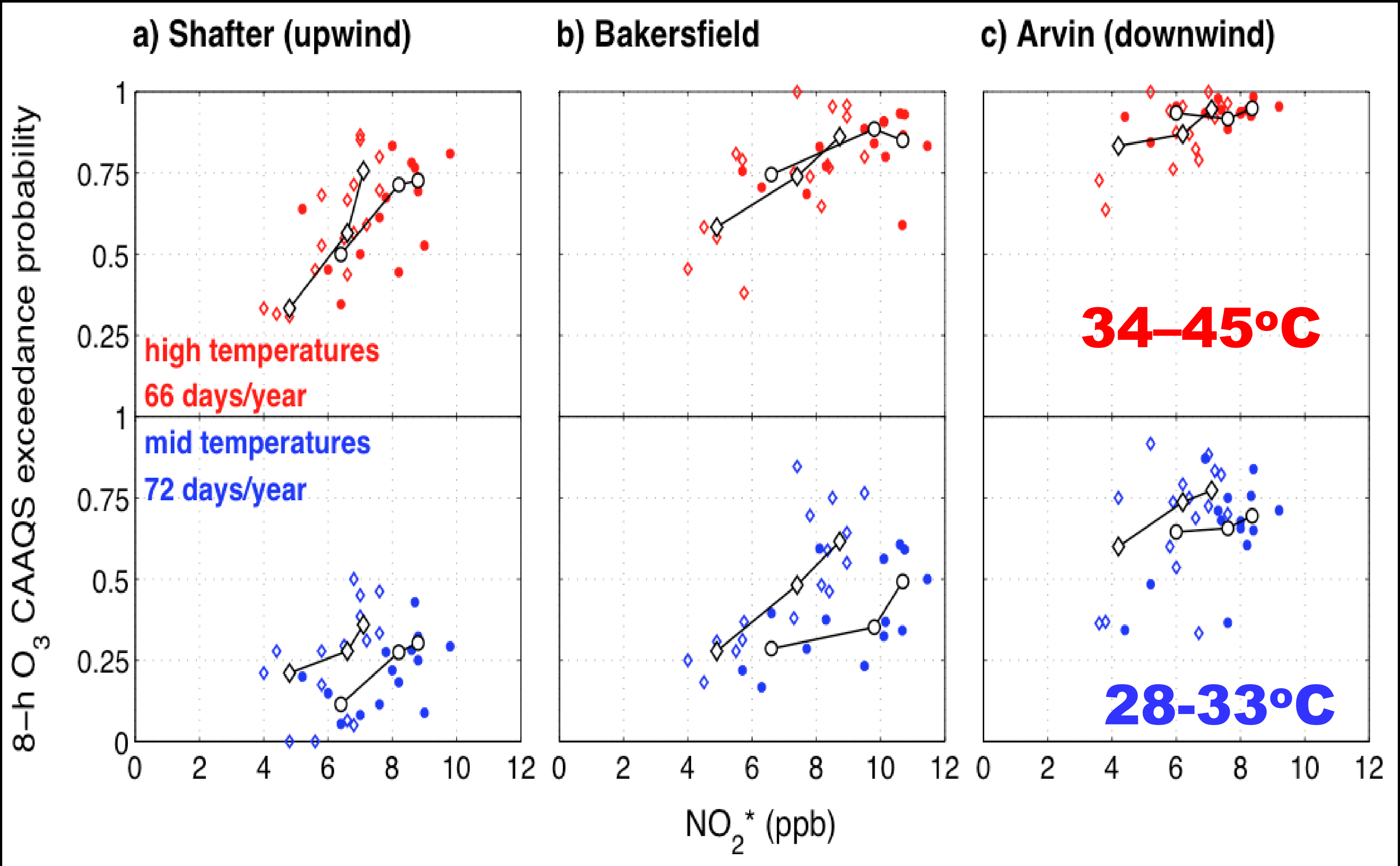
NO_x- HO_x

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

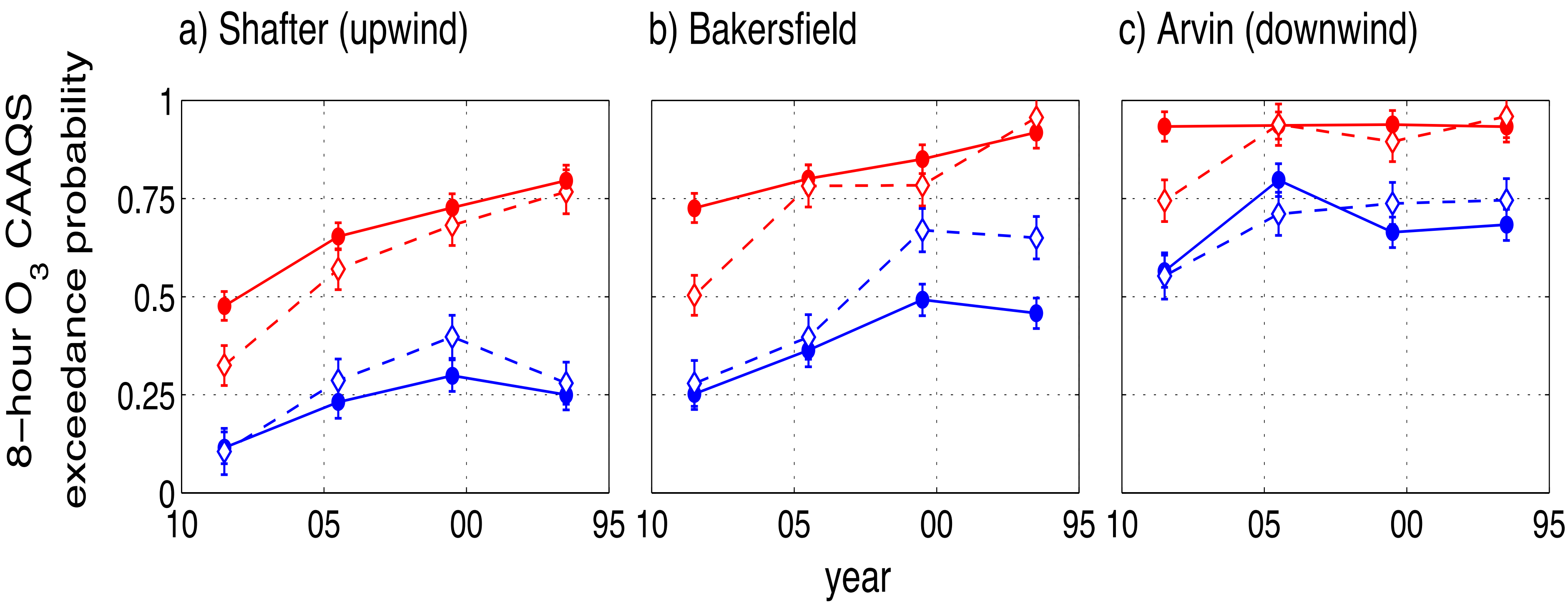
$$RO_2 + NO \xrightarrow{M} RONO_2$$

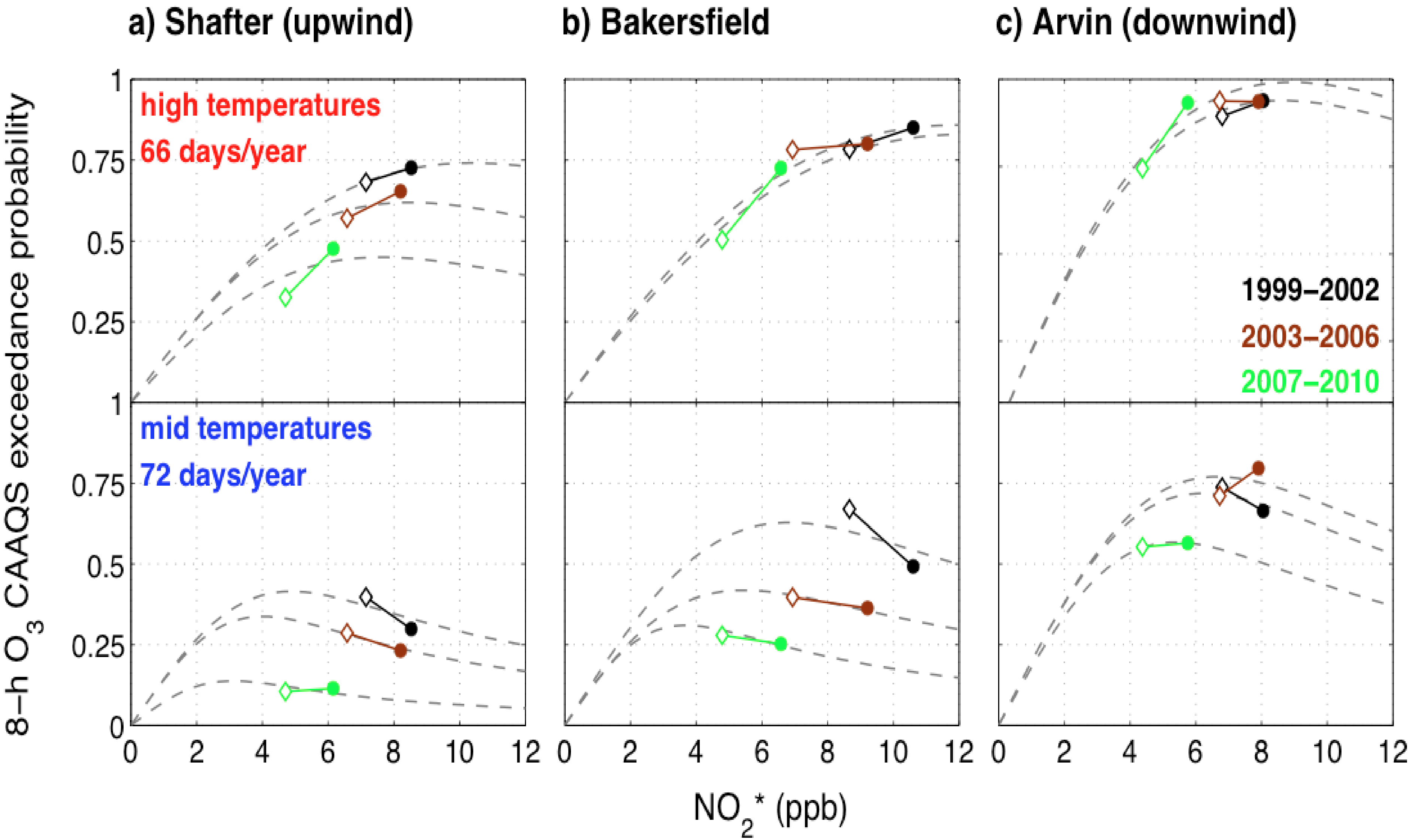
Continental O_3 Production Rates



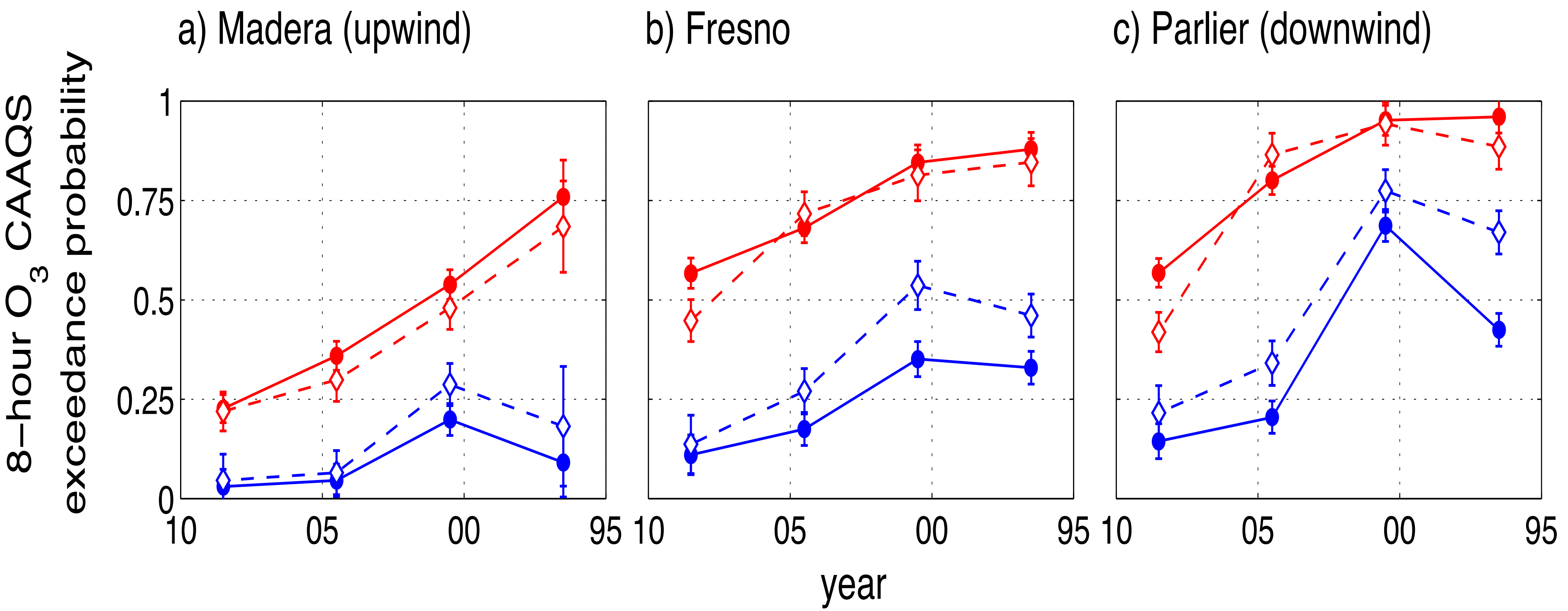


a) Shafter (upwind)
b) Bakersfield
c) Arvin (downwind)
8–h O3 CAAQS exceedance probability
high temperatures
66 days/year
mid temperatures
72 days/year
34–45°C
28-33°C
NO2* (ppb)
0
0.25
0.5
0.75
1
0
2
4
6
8
10
12

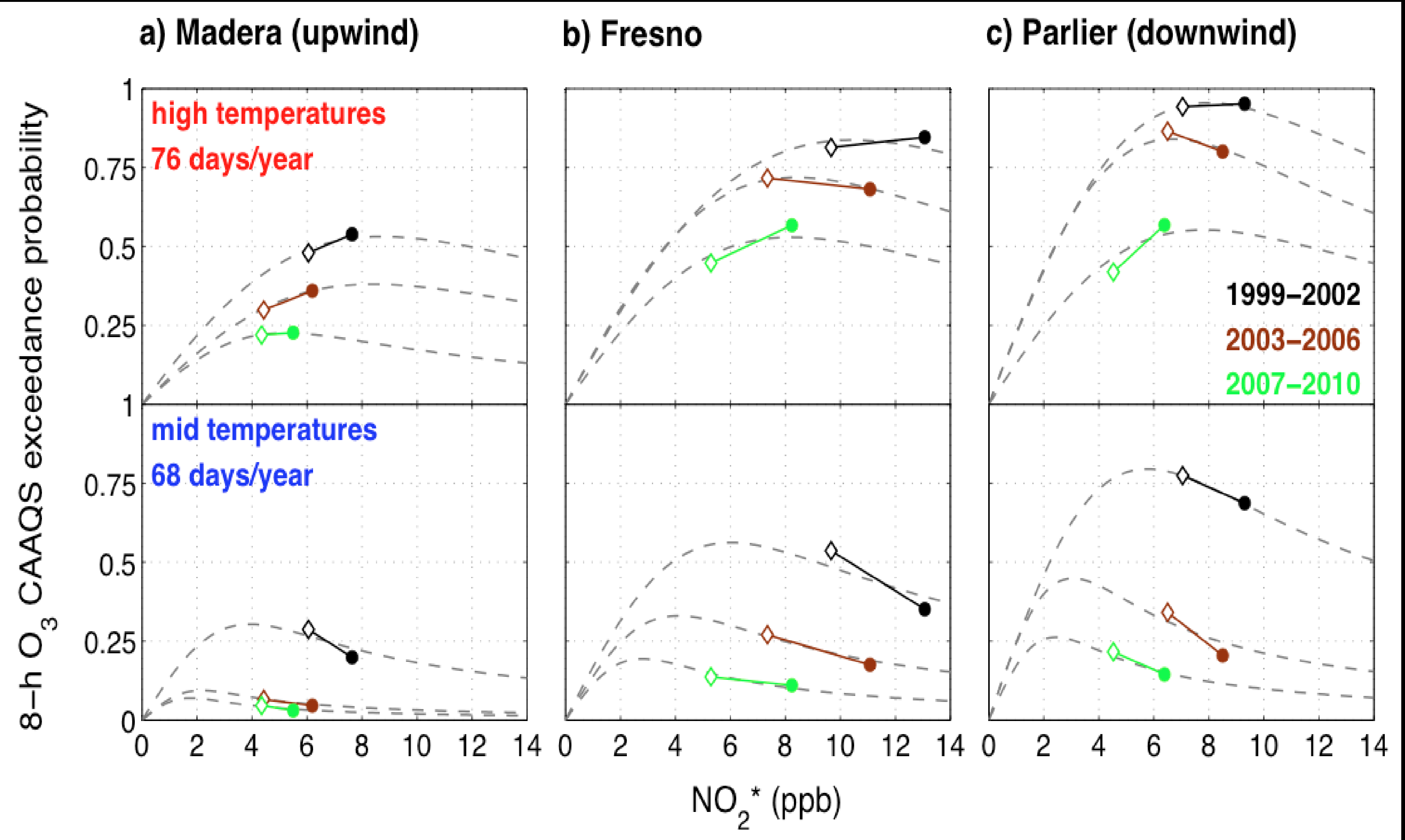

a) Shafter (upwind)
b) Bakersfield
c) Arvin (downwind)
8−hour O3 CAAQS
exceedance probability
1
0.75
0.5
0.25
0
10
05
00
95
year



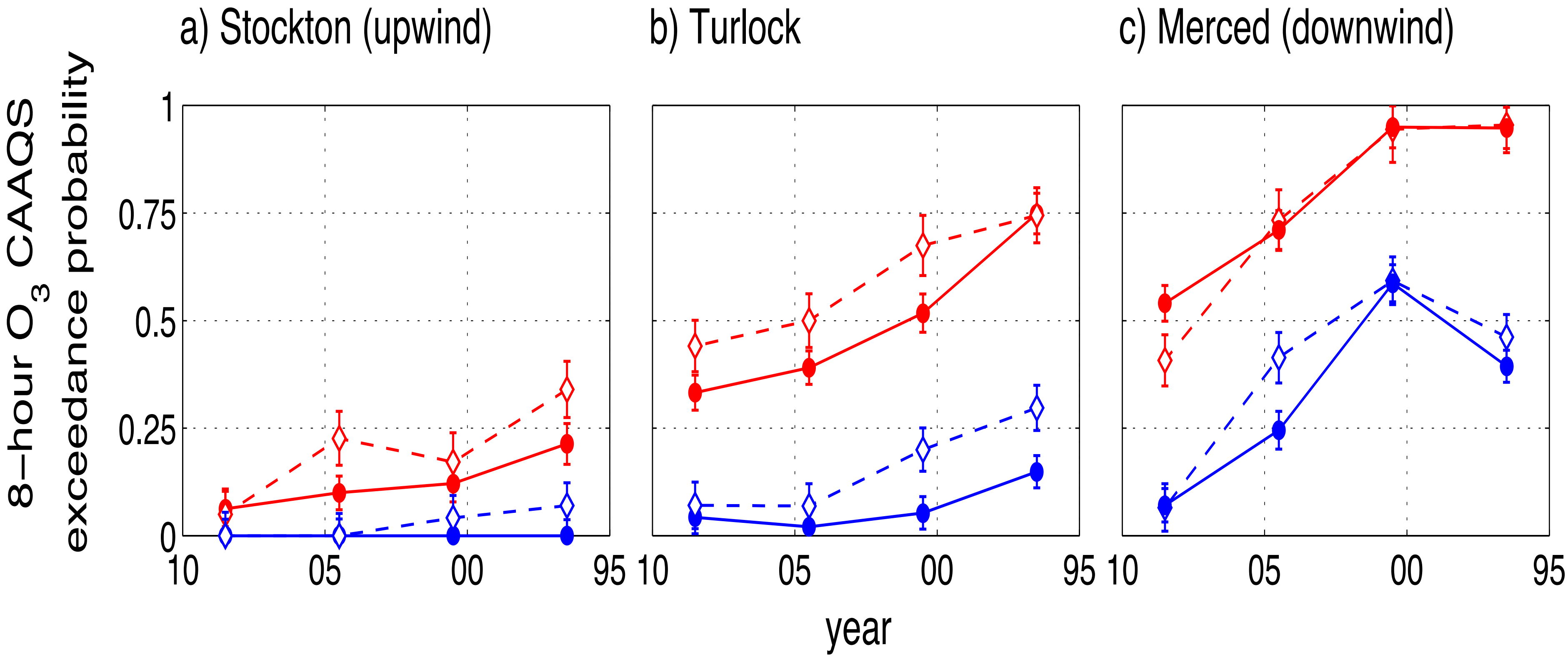
a) Shafter (upwind)
b) Bakersfield
c) Arvin (downwind)
high temperatures
66 days/year
mid temperatures
72 days/year
1999–2002
2003–2006
2007–2010
8–h O3 CAAQS exceedance probability
NO2* (ppb)
0
0.25
0.5
0.75
1
0
2
4
6
8
10
12

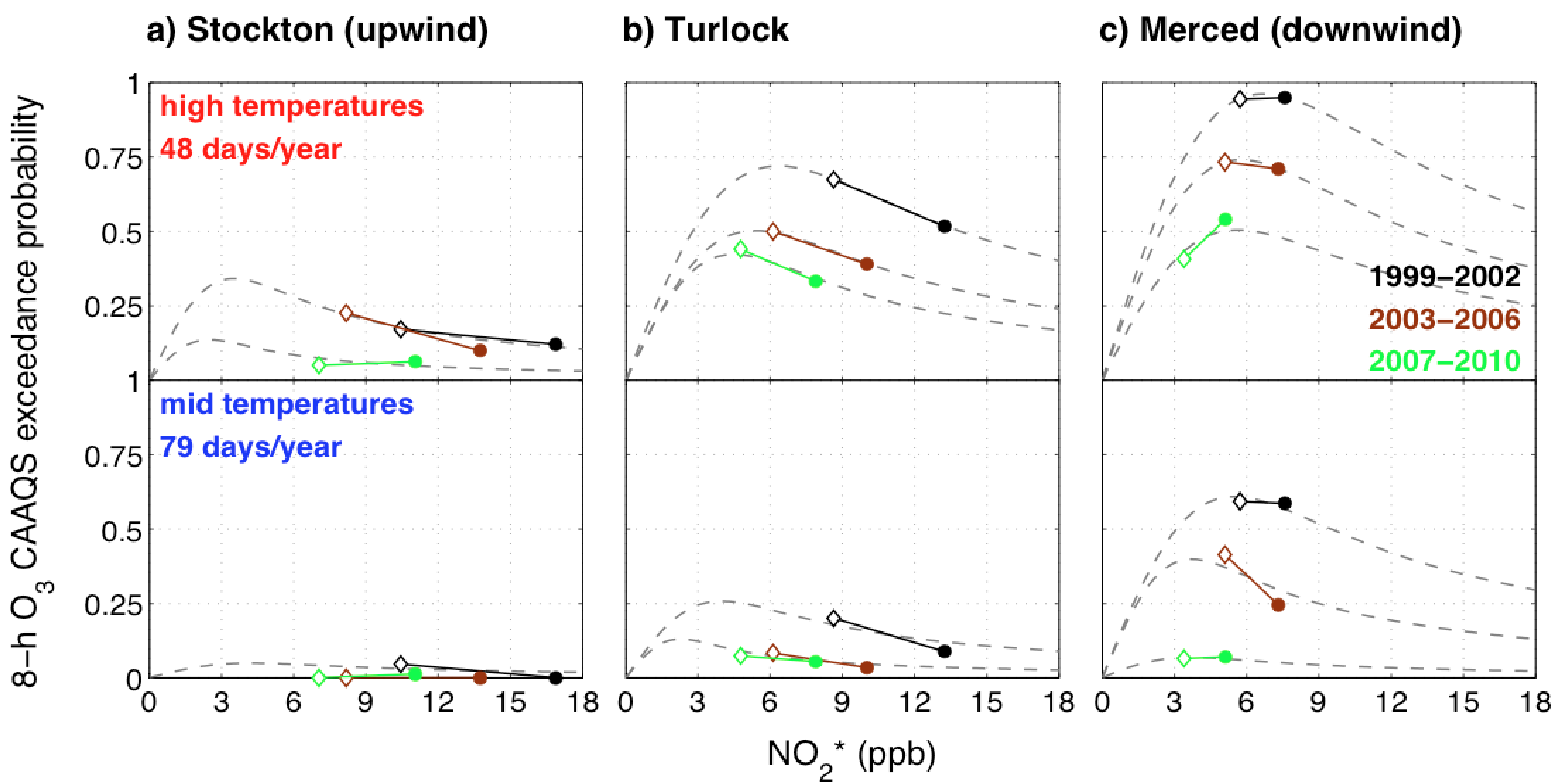


a) Madera (upwind)
b) Fresno
c) Parlier (downwind)
8−hour O3 CAAQS exceedance probability
1
0.75
0.5
0.25
0
10
05
00
95
year



a) Madera (upwind)
b) Fresno
c) Parlier (downwind)
high temperatures
76 days/year
mid temperatures
68 days/year
1999–2002
2003–2006
2007–2010
8–h O_3 CAAQS exceedance probability
NO_2* (ppb)
0
0.25
0.5
0.75
1
0
2
4
6
8
10
12
14


a) Stockton (upwind)
b) Turlock
c) Merced (downwind)
8−hour O_3 CAAQS exceedance probability
1
0.75
0.5
0.25
0
10
05
00
95
year



a) Stockton (upwind)
b) Turlock
c) Merced (downwind)
high temperatures
48 days/year
mid temperatures
79 days/year
1999–2002
2003–2006
2007–2010
8–h O3 CAAQS exceedance probability
NO2* (ppb)
0
0.25
0.5
0.75
1
0
3
6
9
12
15
18

Result #1

Widespread NO_x reductions are approaching the point where ozone reductions will be a direct consequence throughout the SJV (and likely in every US city). The effectiveness has been and will be different at different temperature. At the highest temperatures, where violations of state and federal standards are most frequent, NOx controls will be most effective.

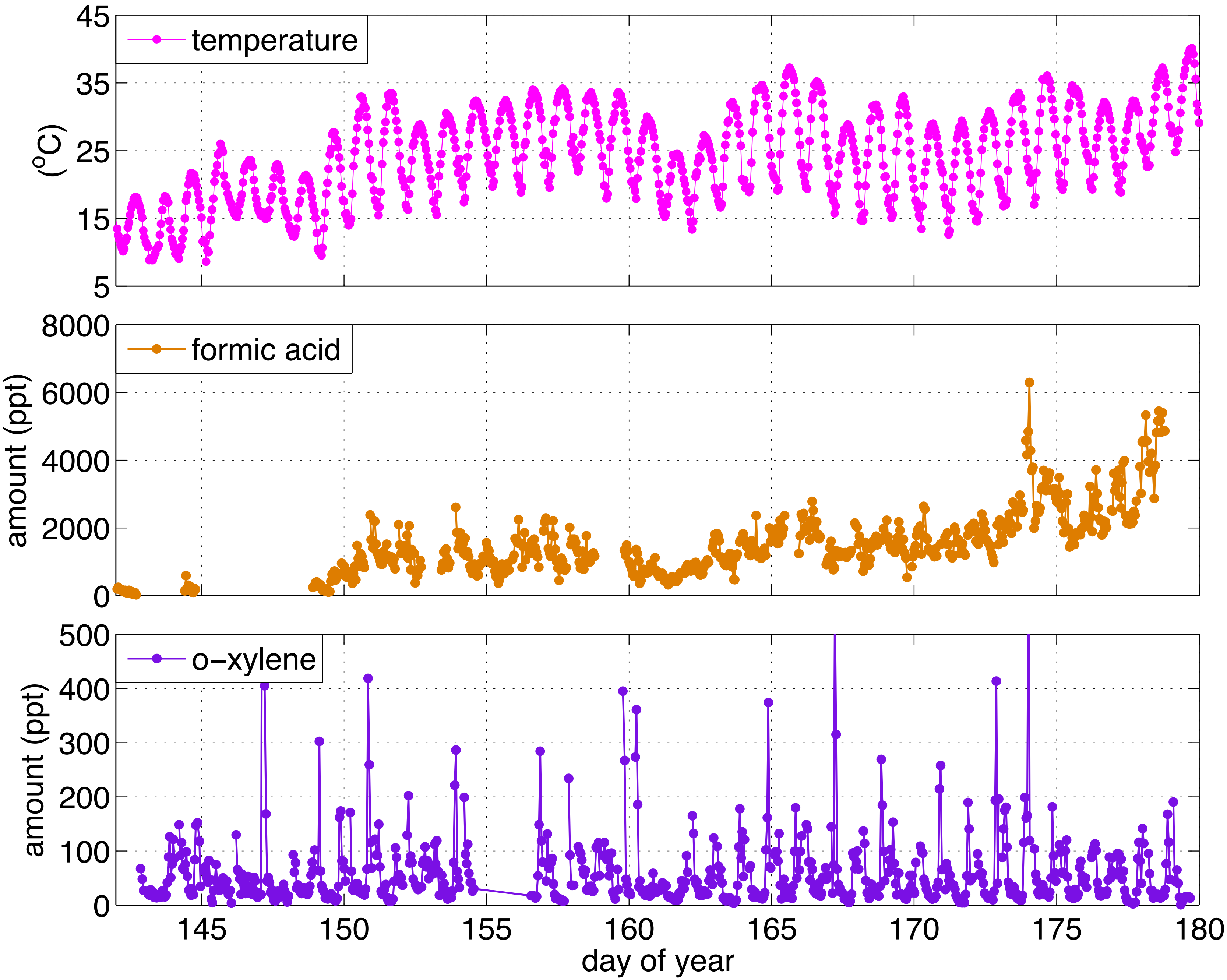
Result #2

VOC controls have been an effective ozone control strategy in the northern and central SJV and at moderate T in the southern SJV, but <u>not at high T</u> at the southern end.

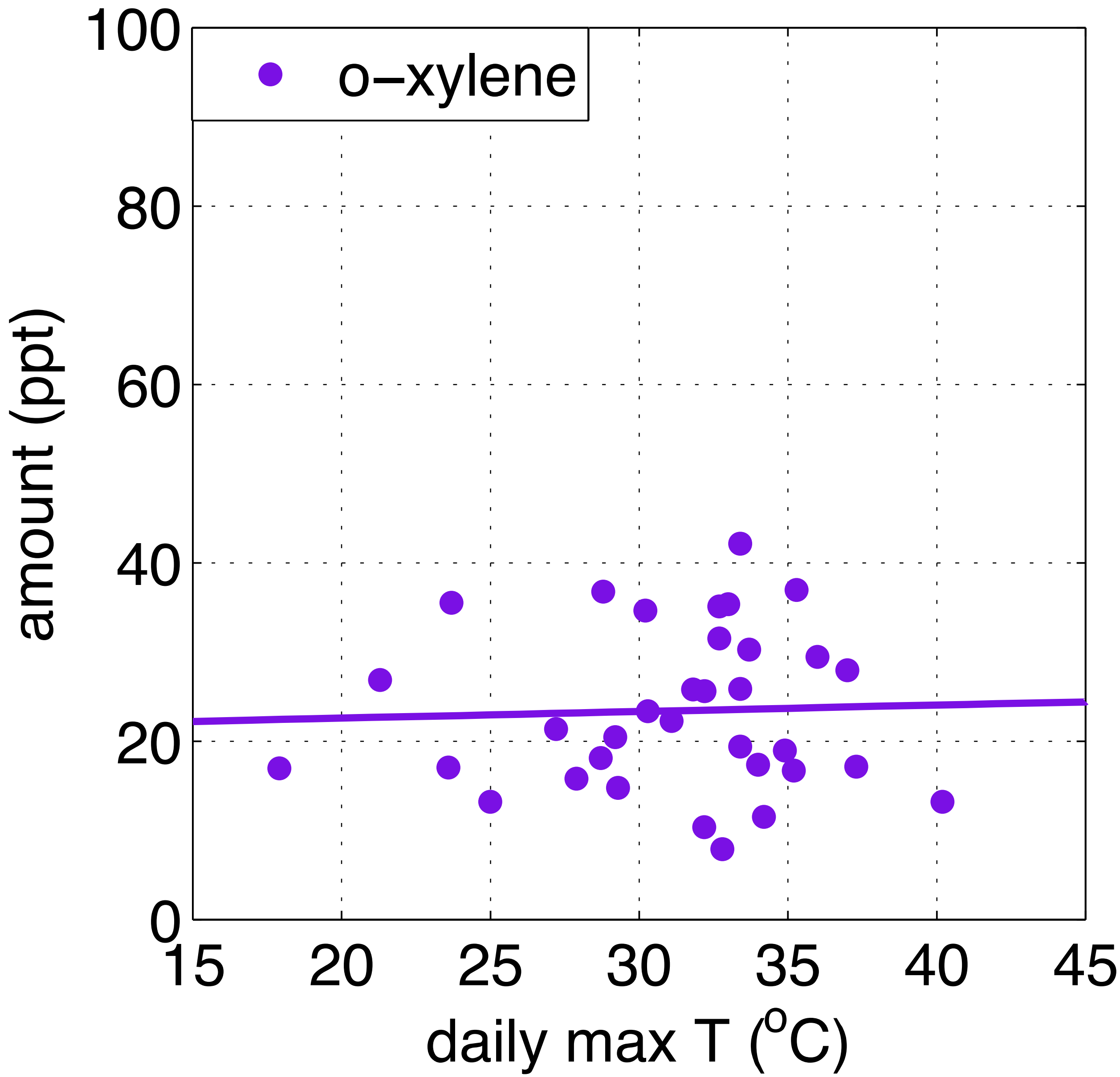
Questions

What is the source of the high T organics?

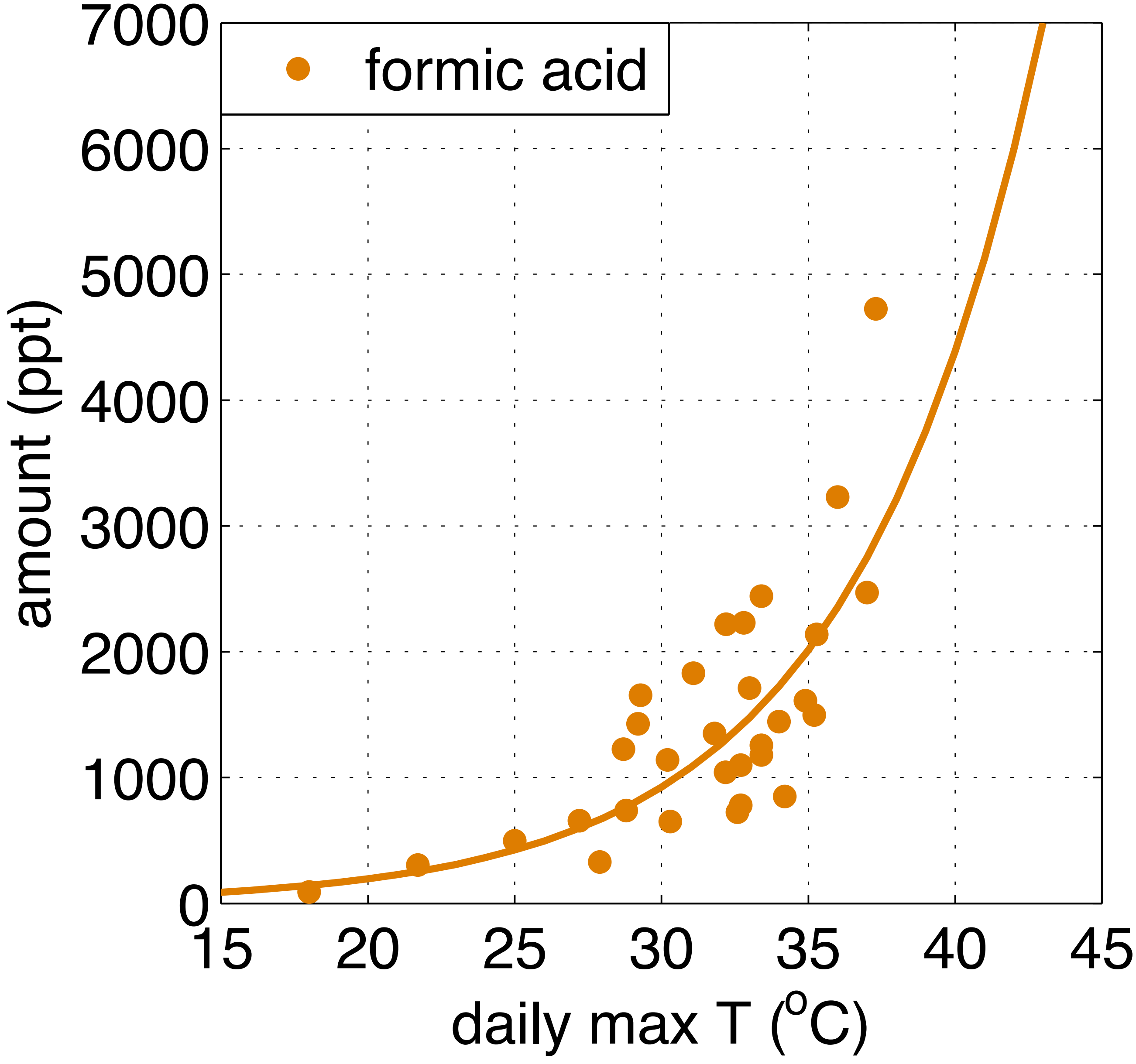
Is it controllable?



temperature
(°C)
45
35
25
15
5
formic acid
amount (ppt)
8000
6000
4000
2000
0
o−xylene
amount (ppt)
500
400
300
200
100
0
145
150
155
160
165
170
175
180
day of year

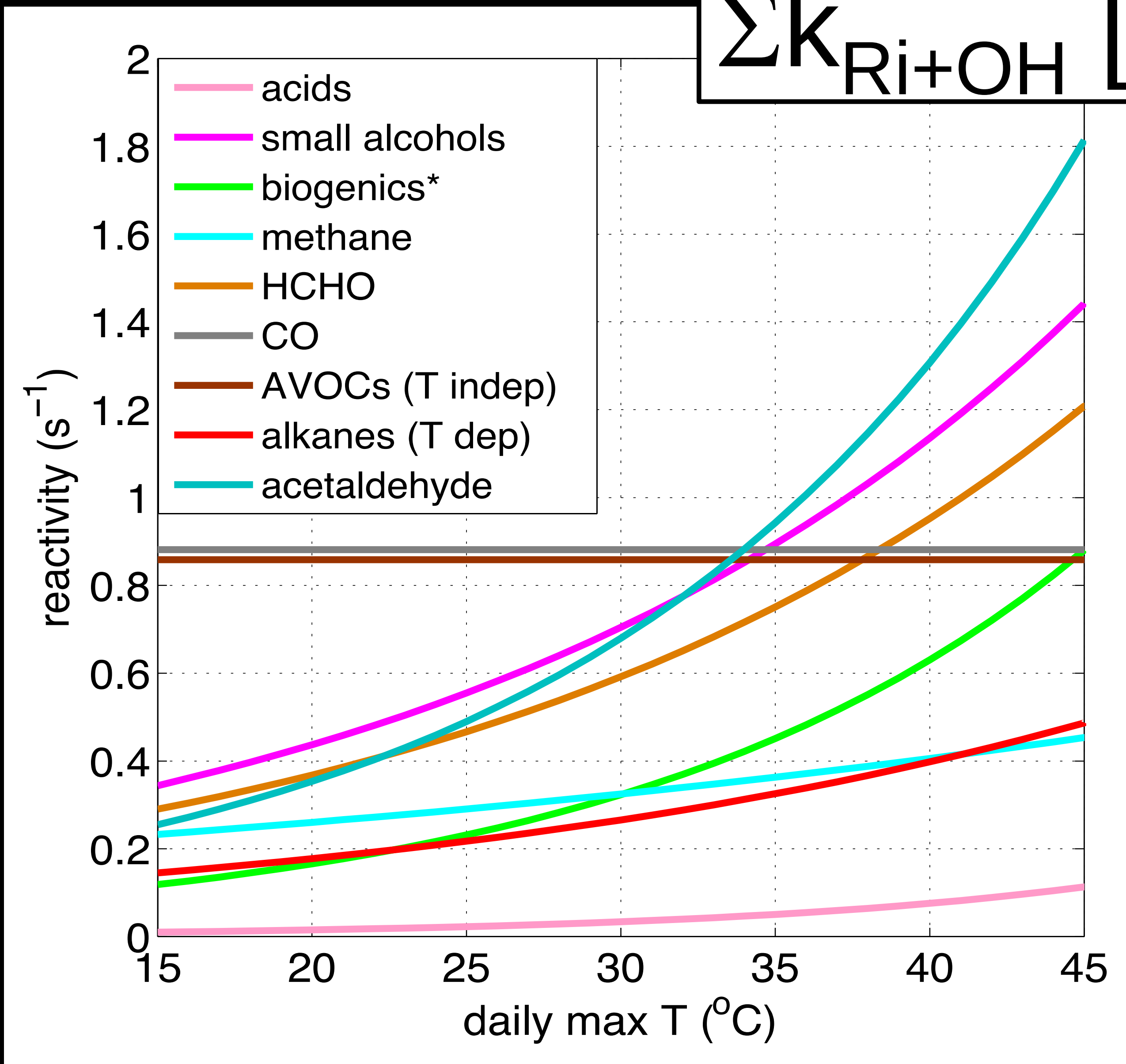


o−xylene
amount (ppt)
100
80
60
40
20
0
15
20
25
30
35
40
45
daily max T (oC)



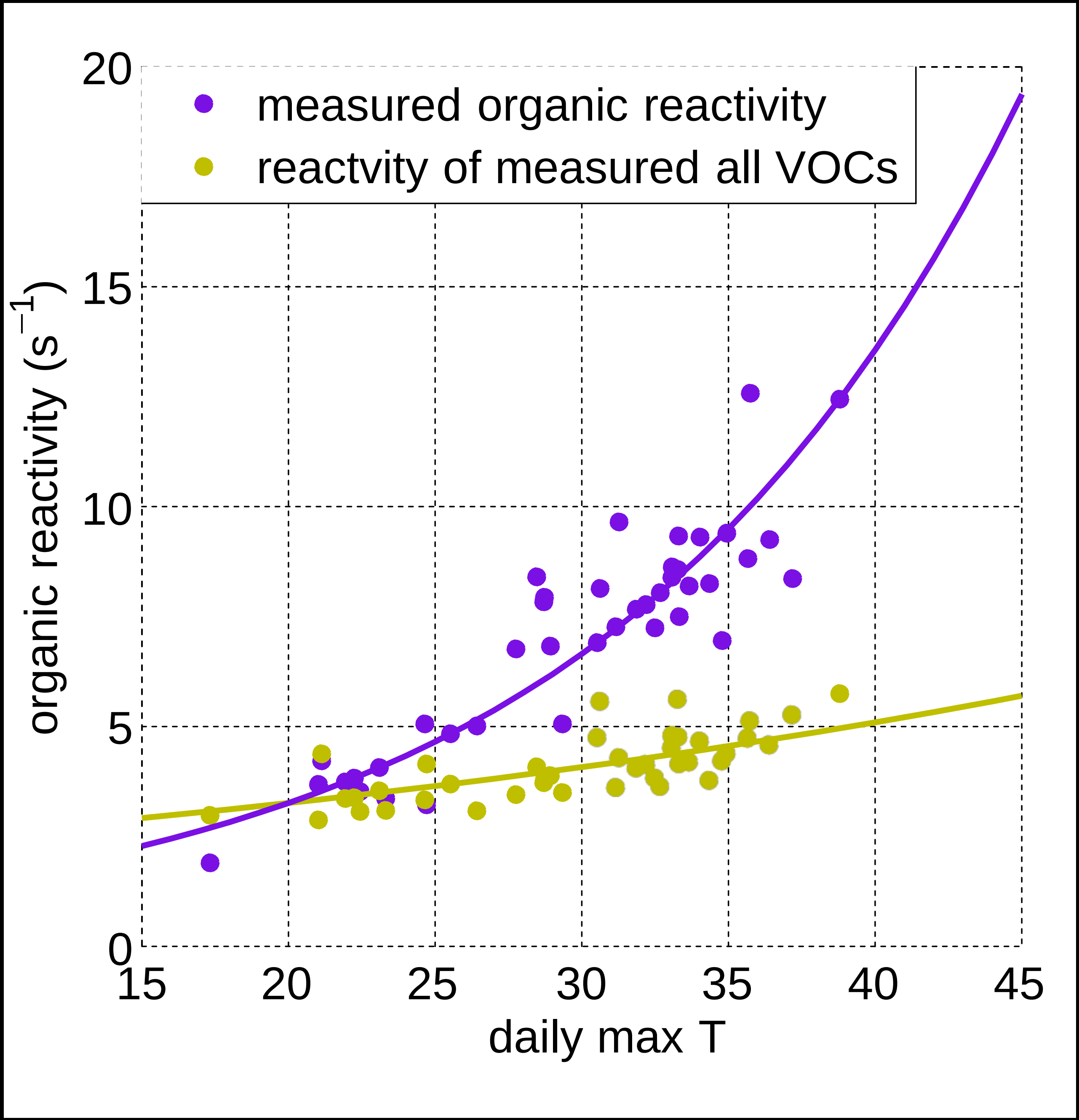
formic acid
amount (ppt)
7000
6000
5000
4000
3000
2000
1000
0
15
20
25
30
35
40
45
daily max T (oC)

$$\Sigma k_{Ri+OH}\ [R_i]$$



Small aldehydes and alcohols

Cars and Trucks



measured organic reactivity
reactvity of measured all VOCs
organic reactivity (s^{-1})
daily max T
20
15
10
5
0
15
20
25
30
35
40
45

Result #3

The VOC that are most important at high temperatures in the southern SJV are small aldehydes and alcohols. These molecules have been discussed (by others) as important emissions from silage.

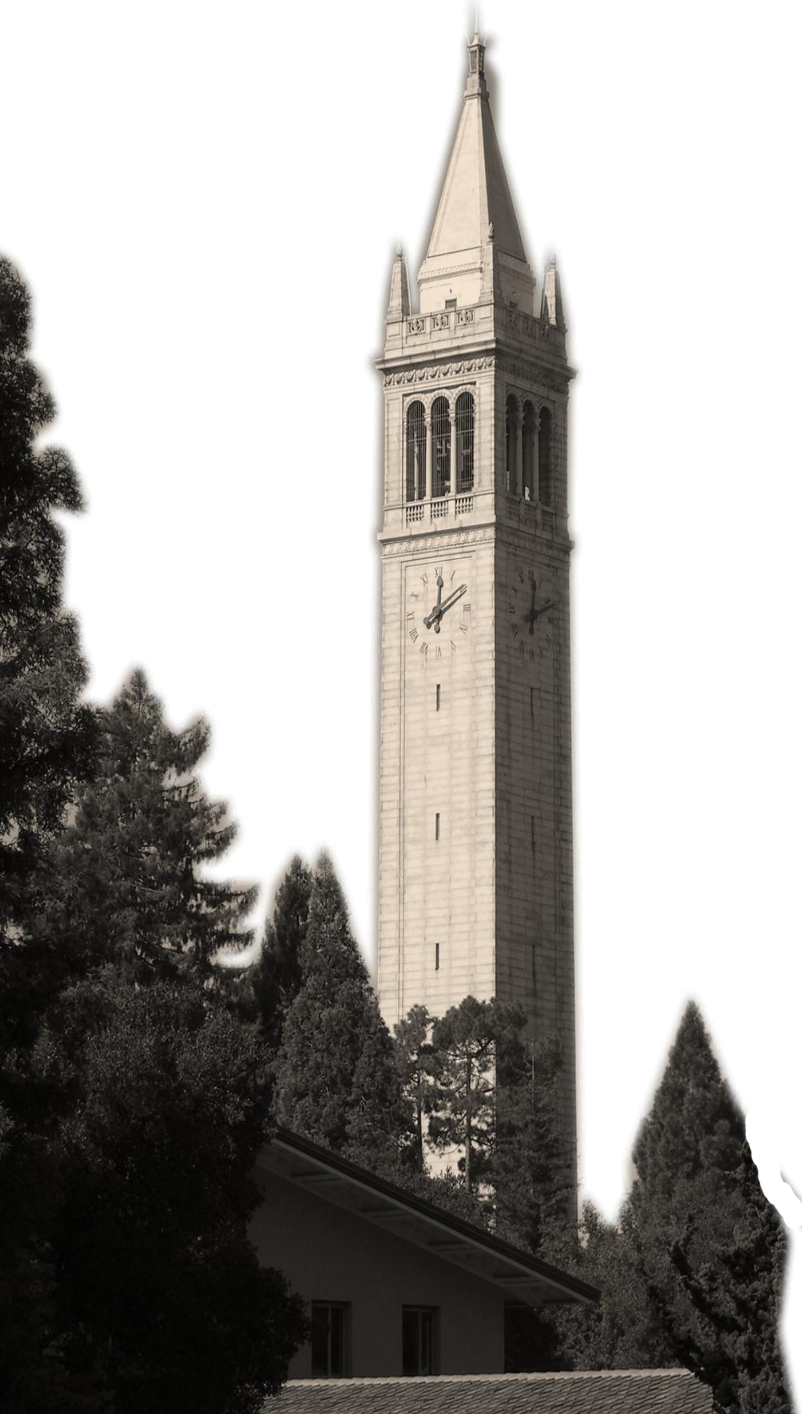
I do not believe that we have a sufficient understanding of where these molecules come from and why they are so strongly temperature dependent to design a control strategy aimed at VOC in the southern SJV.

Thus, NO_x controls are currently the only option for reducing high T violations of the ozone standard in the SJV.

Policy Relevant Conclusion

I do not believe that we have a sufficient understanding of where these molecules come from and why they are so strongly temperature dependent to design a control strategy aimed at VOC in the southern SJV.

Thus, NO_x controls are currently the only option for reducing high T violations of the ozone standard in the SJV.



Overview

O_3 trends vs. NO_x and VOC Controls

$RONO_2$ content of aerosol

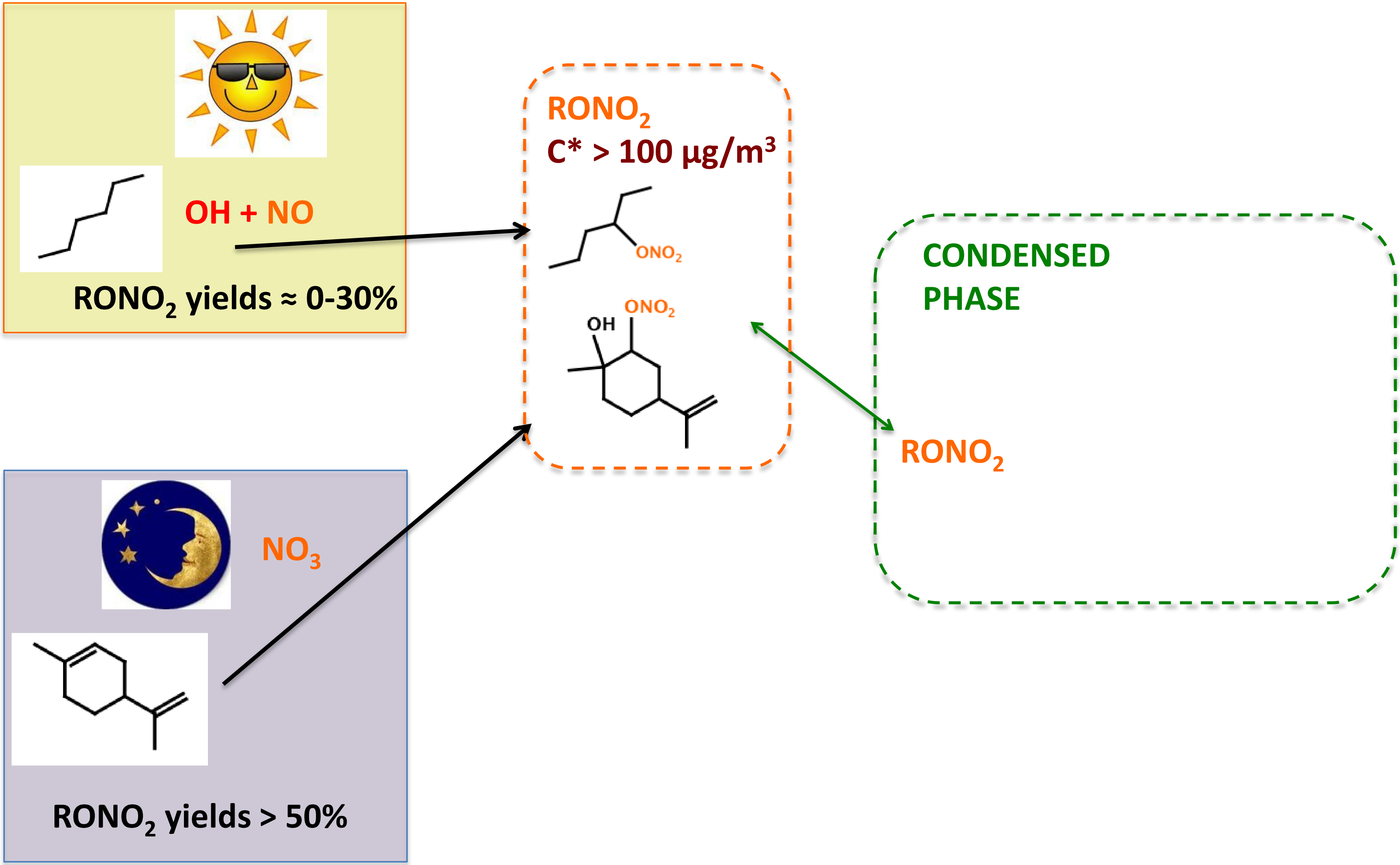
Questions

Have the dramatic NO_x reductions affected aerosol?

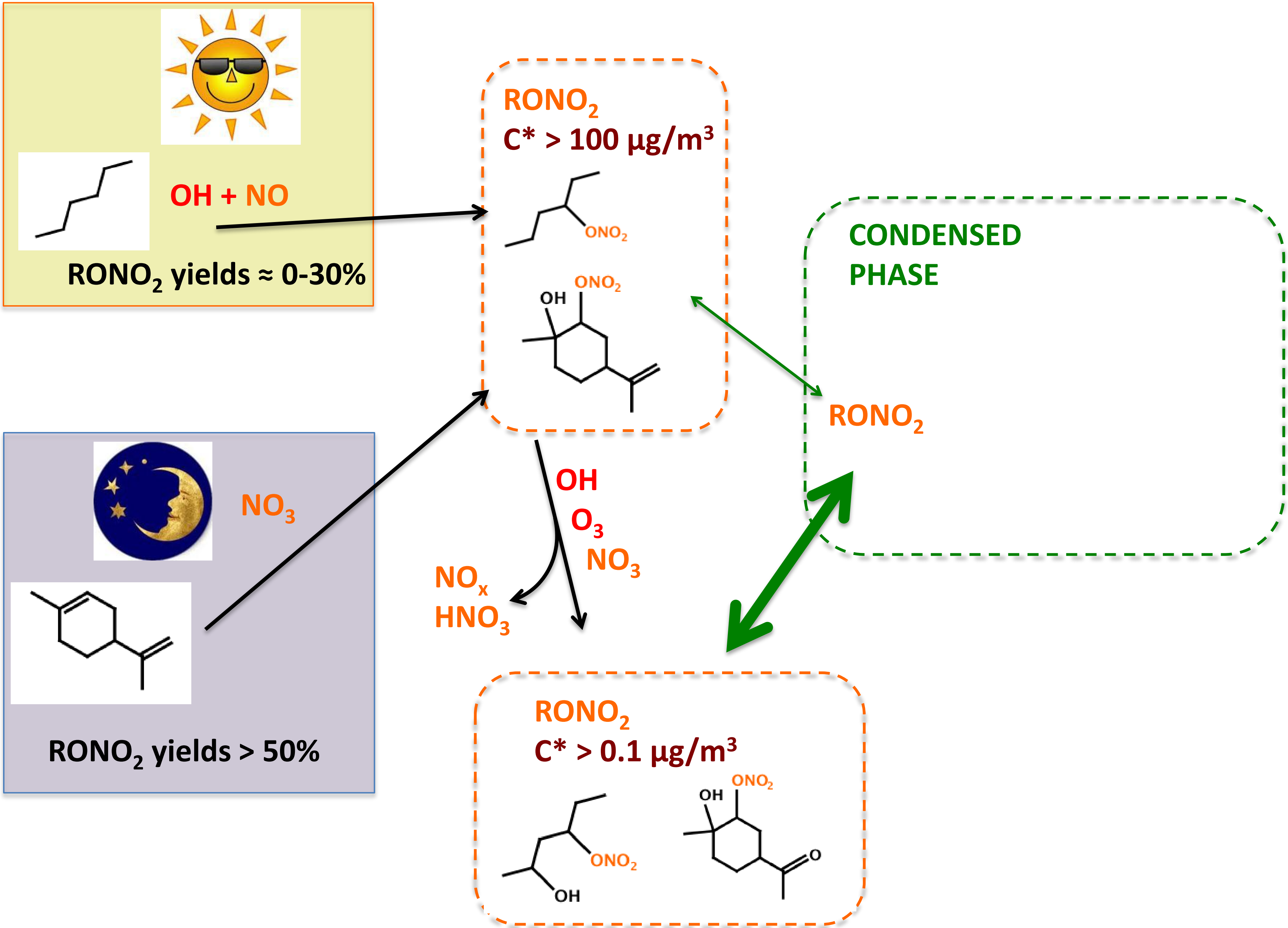
What role (if any) does $RONO_2$ play in aerosol?

Drew Rollins

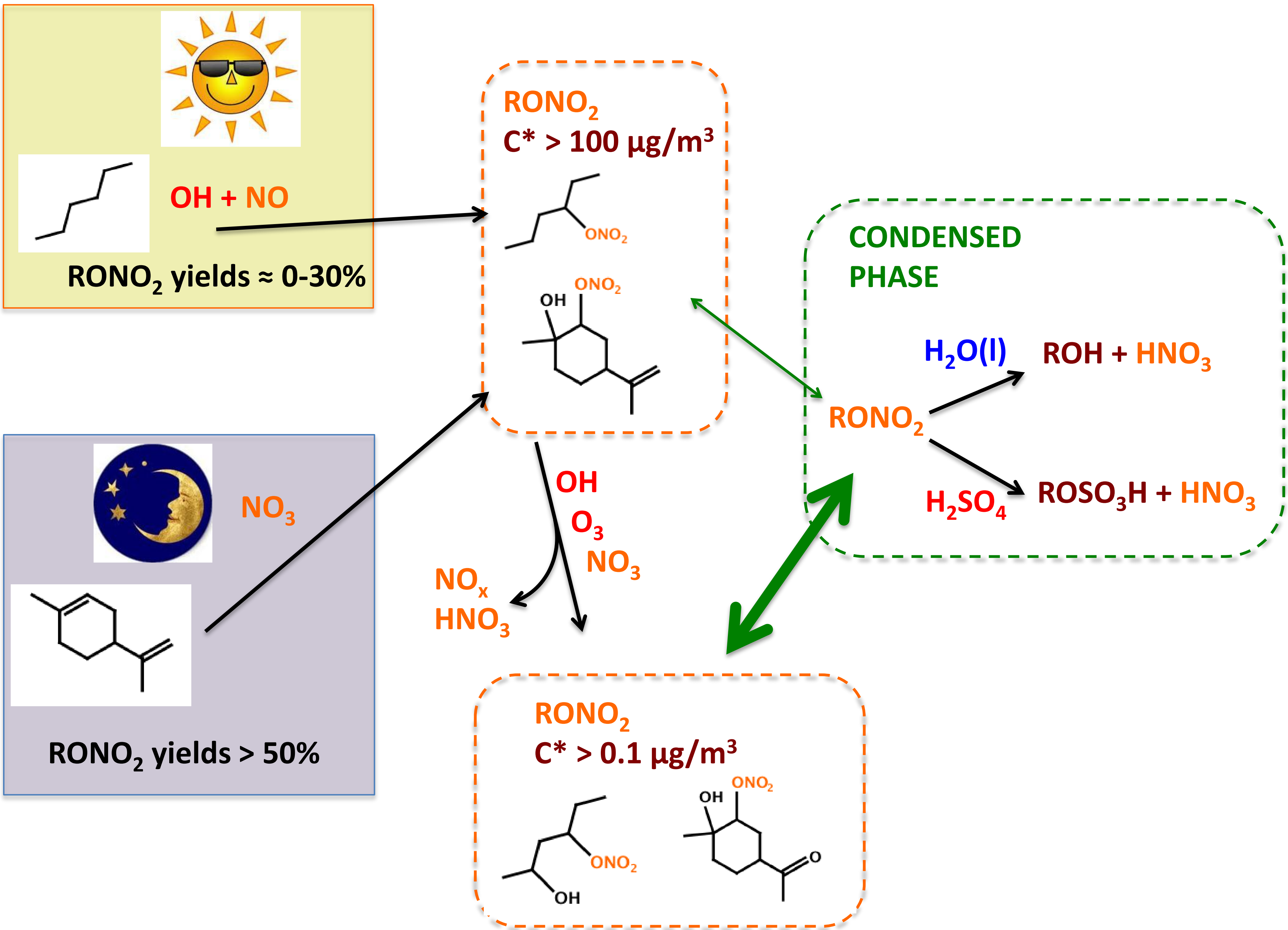
Rollins et al., Science, 2012 and JGR in review

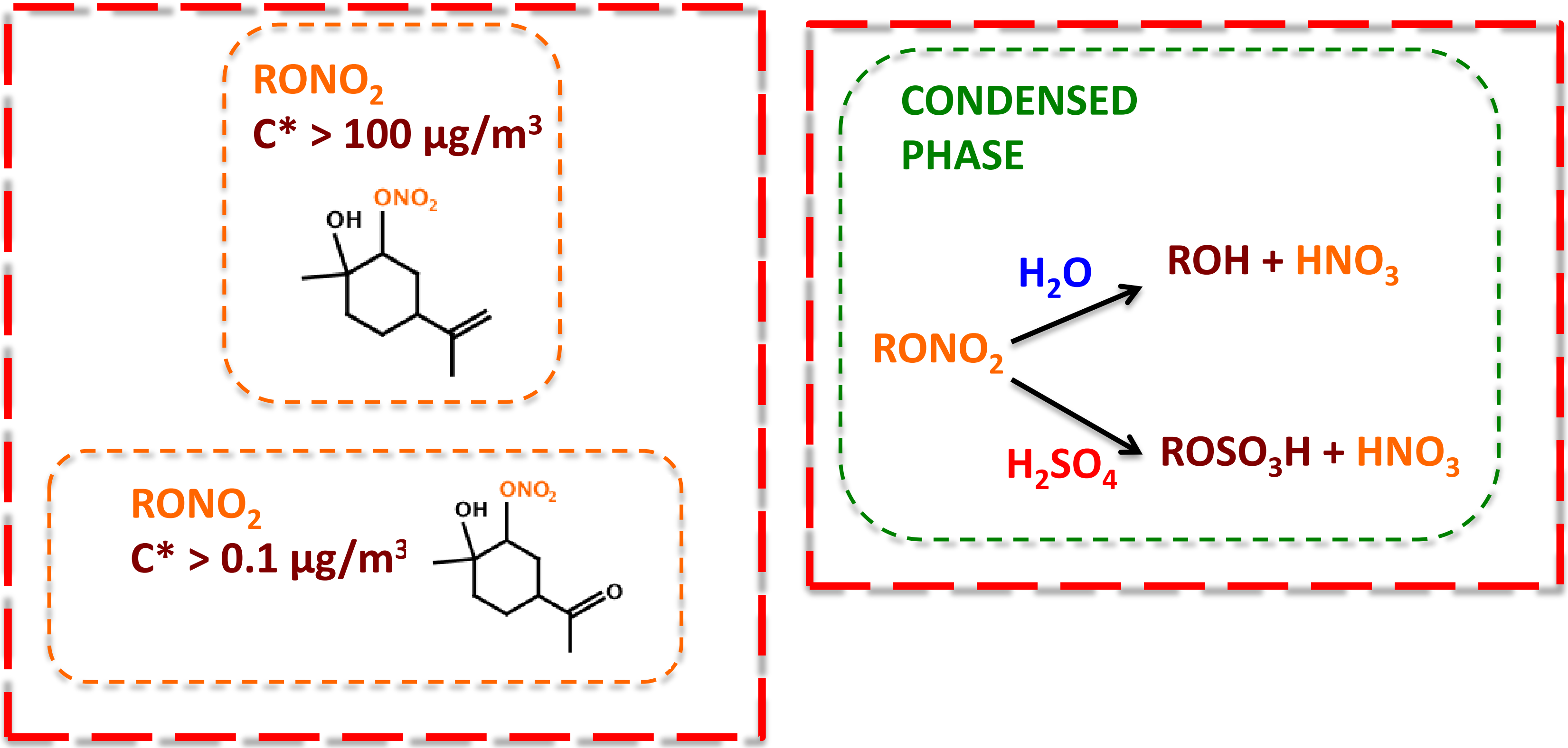


OH + NO
RONO2 yields ≈ 0-30%
NO3
RONO2 yields > 50%
RONO2
C* > 100 µg/m3
ONO2
OH
ONO2
CONDENSED PHASE
RONO2



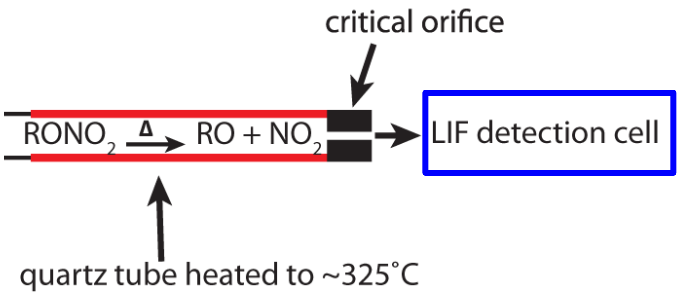
OH + NO
RONO2 yields ≈ 0-30%
NO3
RONO2 yields > 50%
RONO2
C* > 100 µg/m3
ONO2
OH
ONO2
OH
O3
NO3
NOx
HNO3
CONDENSED
PHASE
RONO2
RONO2
C* > 0.1 µg/m3
ONO2
OH
OH
ONO2
O


OH + NO
$RONO_2$ yields ≈ 0-30%
$RONO_2$
$C^* > 100\ \mu g/m^3$
ONO_2
OH
ONO_2
CONDENSED
PHASE
$H_2O(l)$
ROH + HNO_3
$RONO_2$
H_2SO_4
$ROSO_3H$ + HNO_3
NO_3
$RONO_2$ yields > 50%
OH
O_3
NO_3
NO_x
HNO_3
$RONO_2$
$C^* > 0.1\ \mu g/m^3$
ONO_2
OH
OH
ONO_2
O



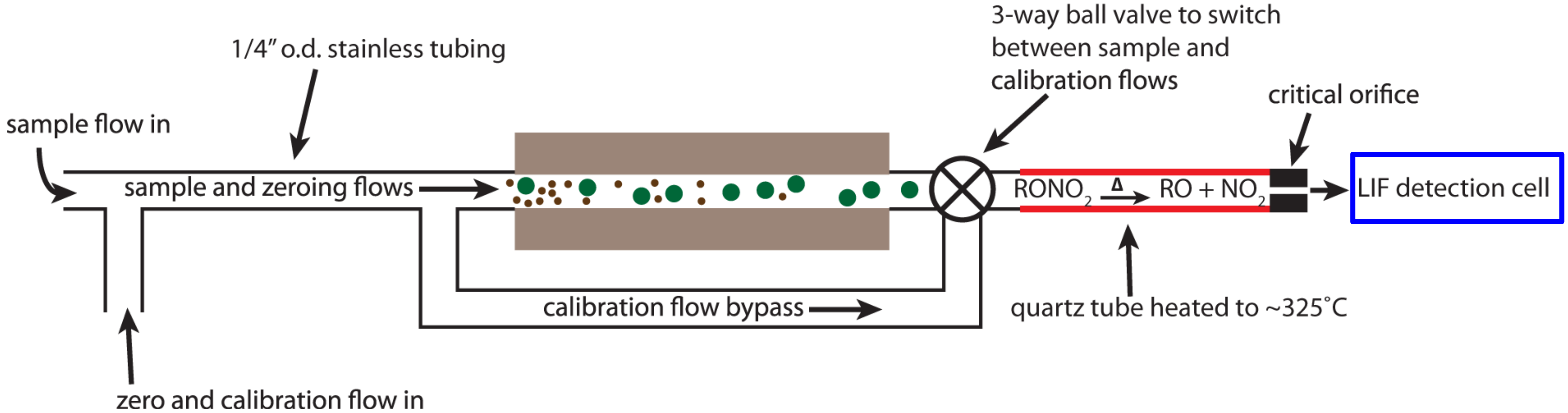
- **2 measurements:**
  - **Particle ΣAN**
  - **Gas + particle ΣAN**
- **Measurements of gas/particle partitioning of ΣAN contain information about large suite of oxidized organics spanning wide range of P_{vap}.**

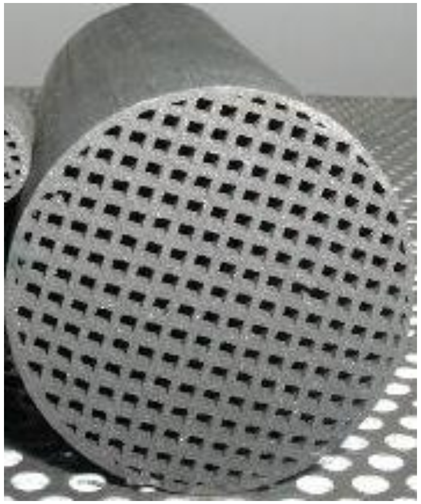
Thermal Dissociation Laser Induced Fluorescence (TD-LIF)



- Detection limit = 100 ng m^{-3} min^{-1}
- Simple, easily automated calibration using NO_2 standard

Thermal Dissociation Laser Induced Fluorescence (TD-LIF)





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- Simple, easily automated calibration using NO_2 standard

A. W. Rollins et al. *Environ. Sci. Technol.* 44, 5540-5545, 2010

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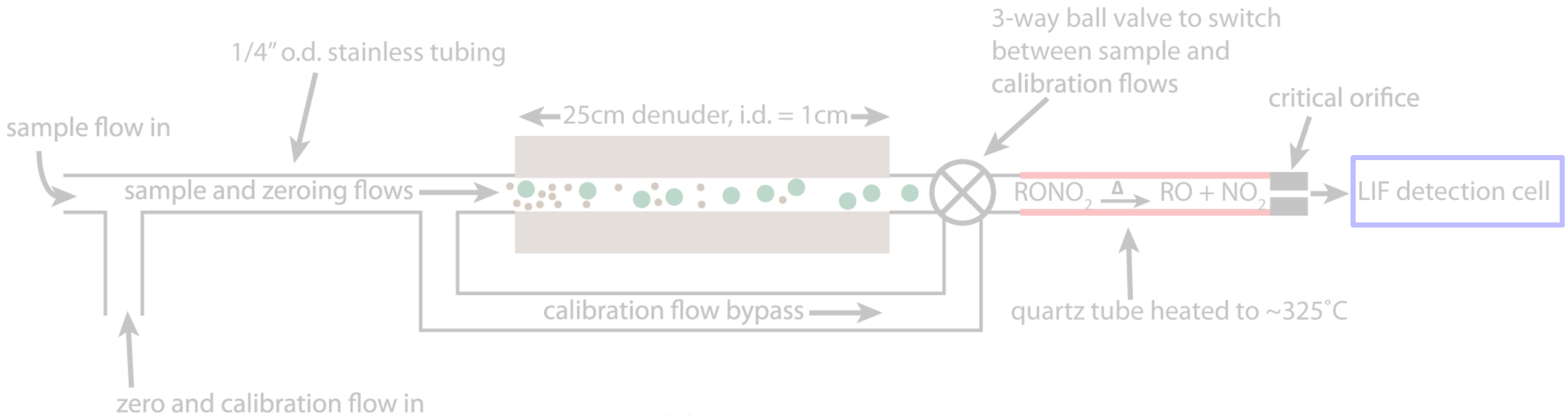
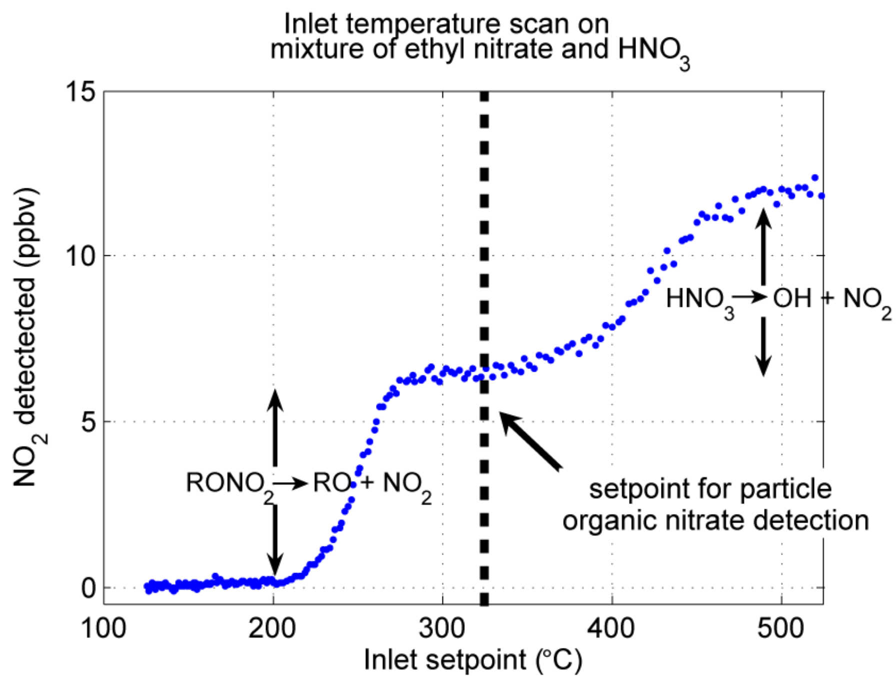


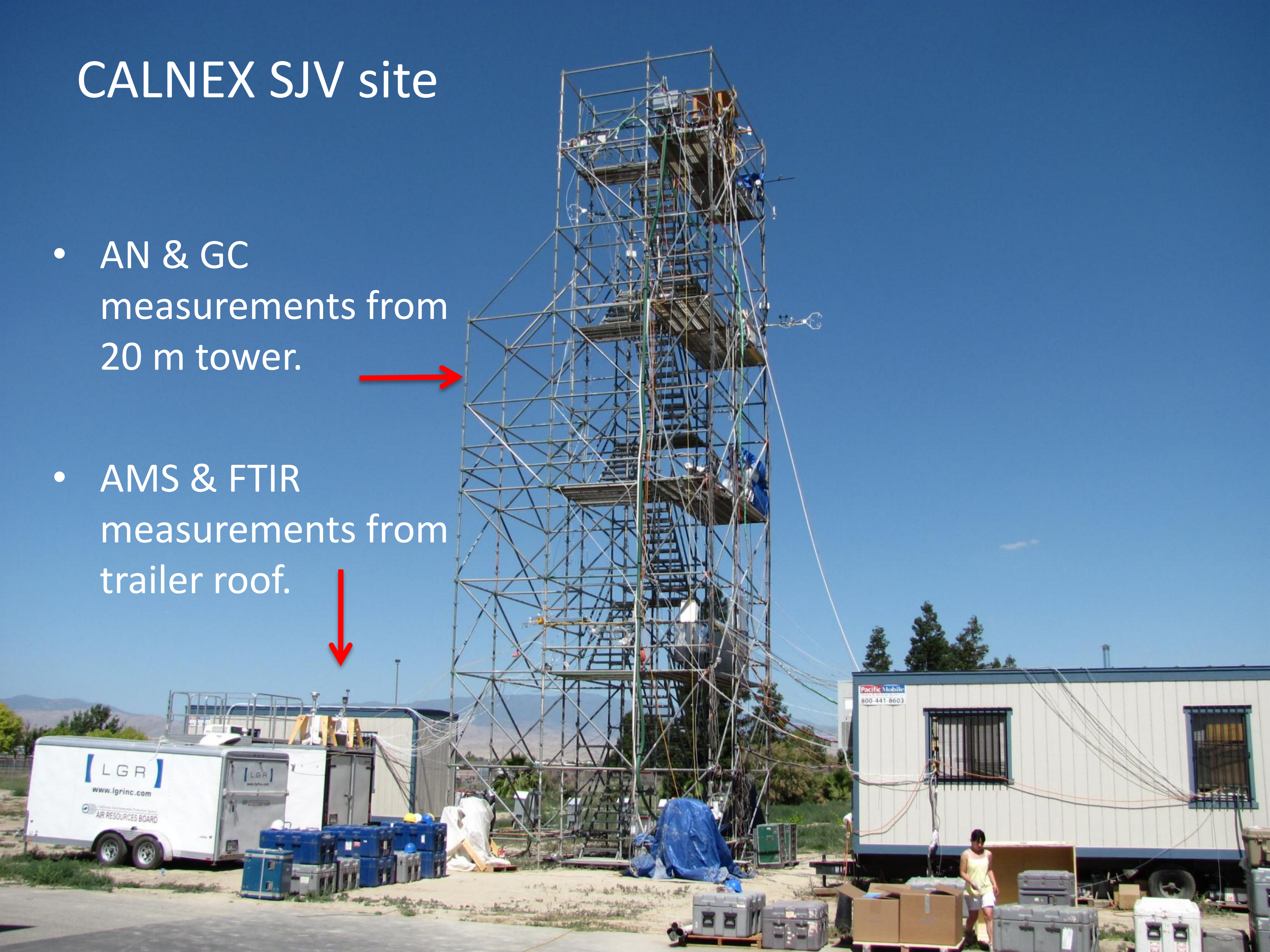


No NO_3^- interference

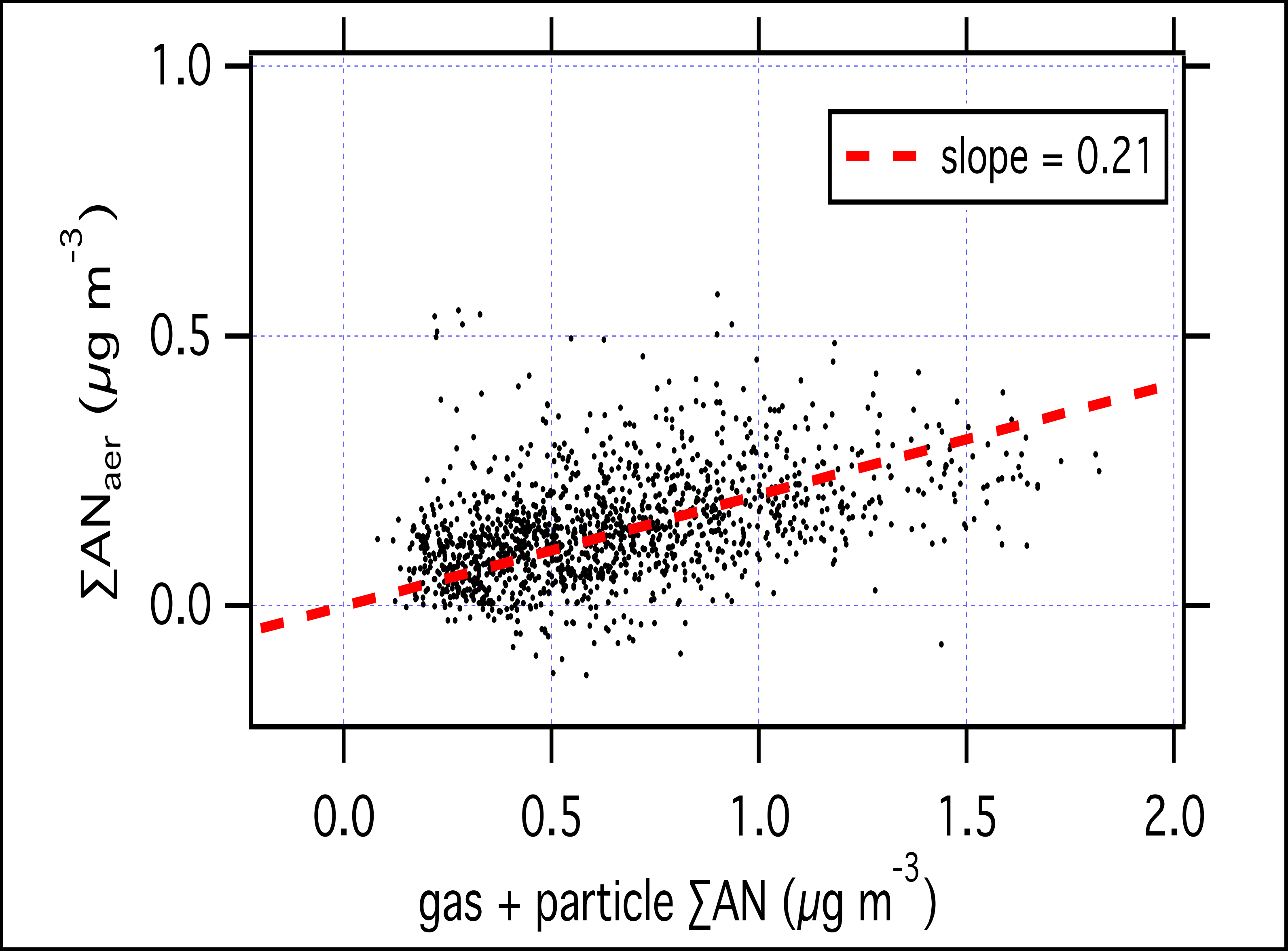
A. W. Rollins et al. *Environ. Sci. Technol.* 44, 5540-5545, 2010

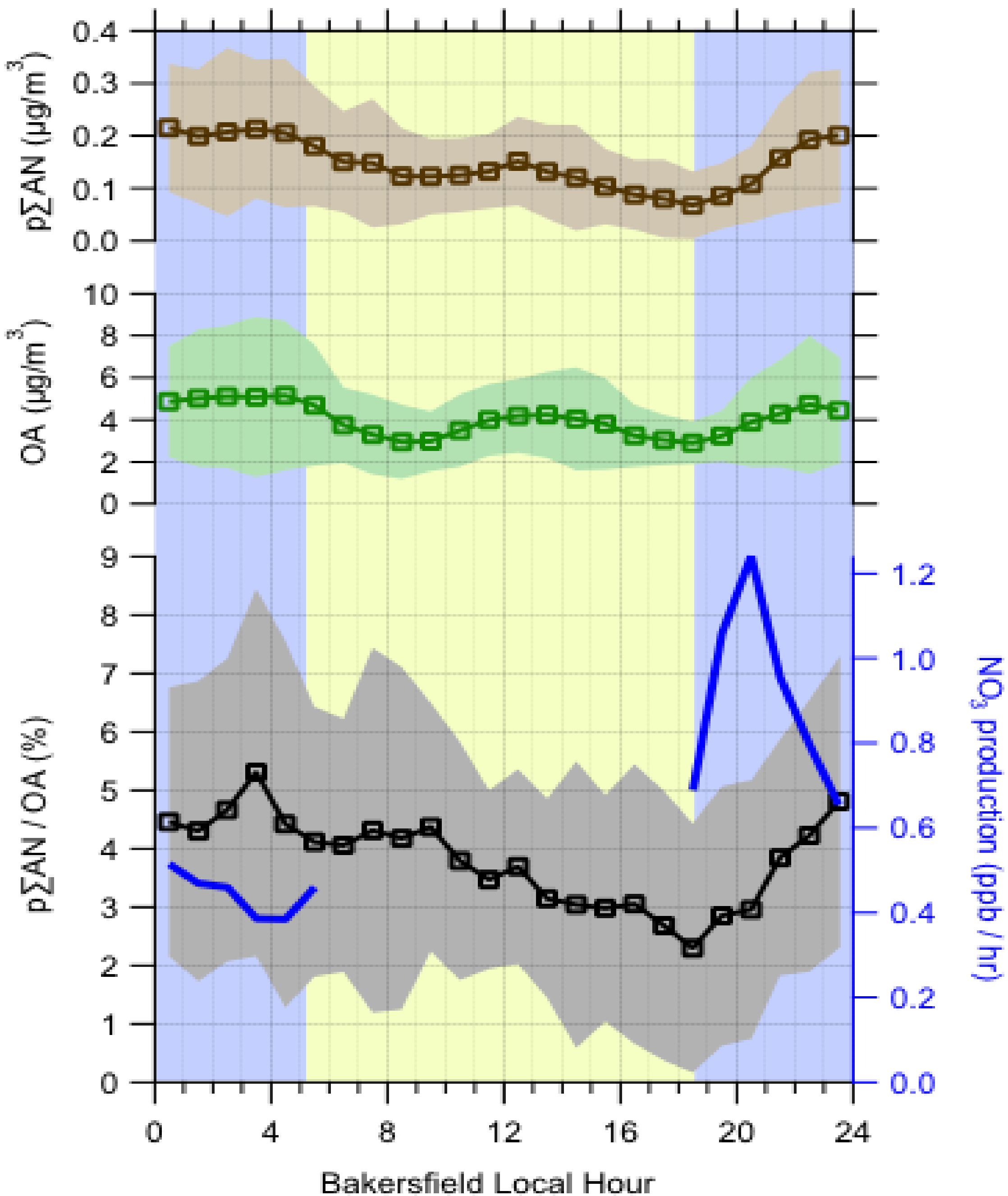
CALNEX SJV site

- AN & GC measurements from 20 m tower.
- AMS & FTIR measurements from trailer roof.

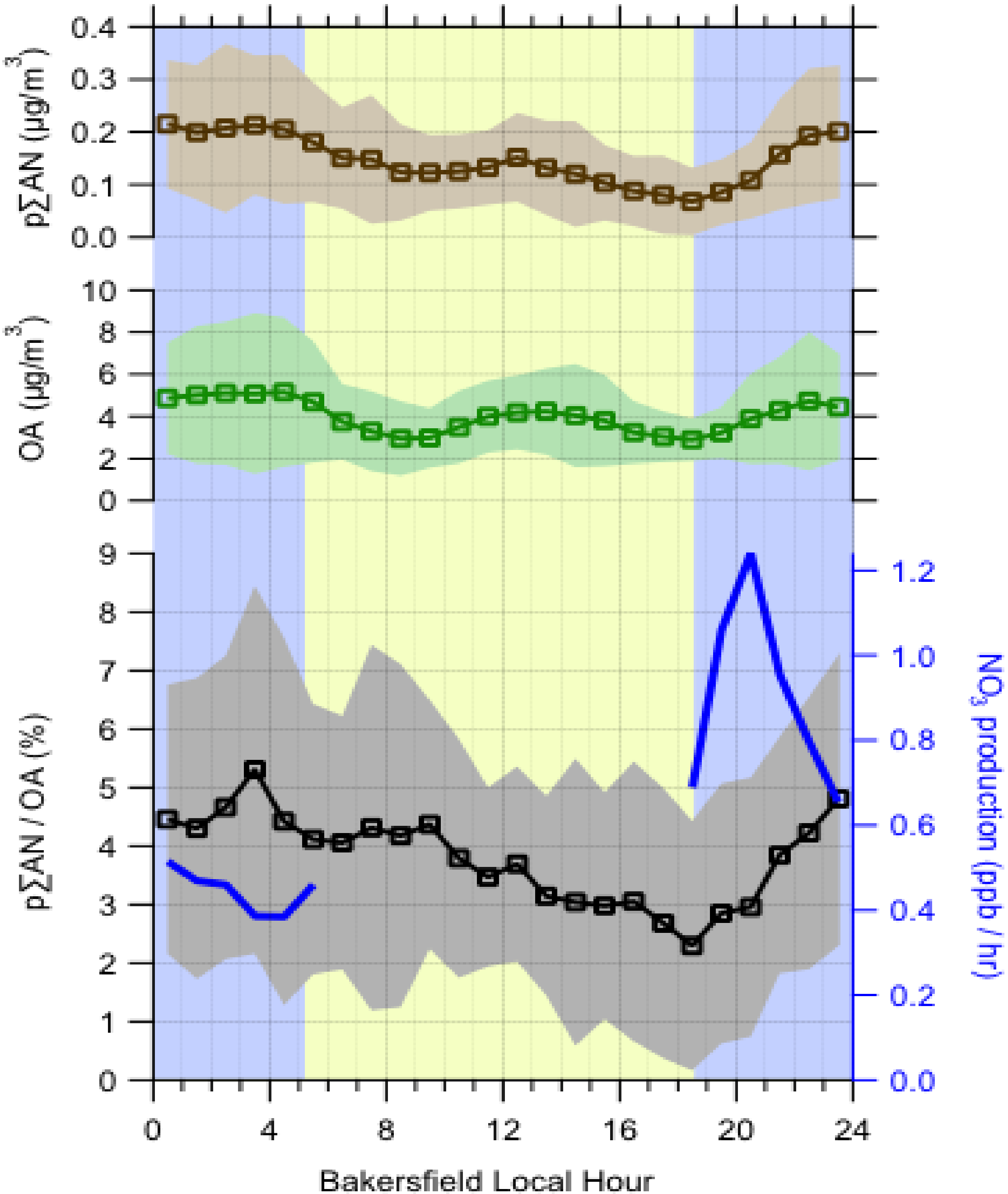


21% of ΣANs are in the condensed phase





pΣAN (µg/m³)
0.4
0.3
0.2
0.1
0.0
OA (µg/m³)
10
8
6
4
2
0
pΣAN / OA (%)
9
8
7
6
5
4
3
2
1
0
NO₃ production (ppb / hr)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
4
8
12
16
20
24
Bakersfield Local Hour



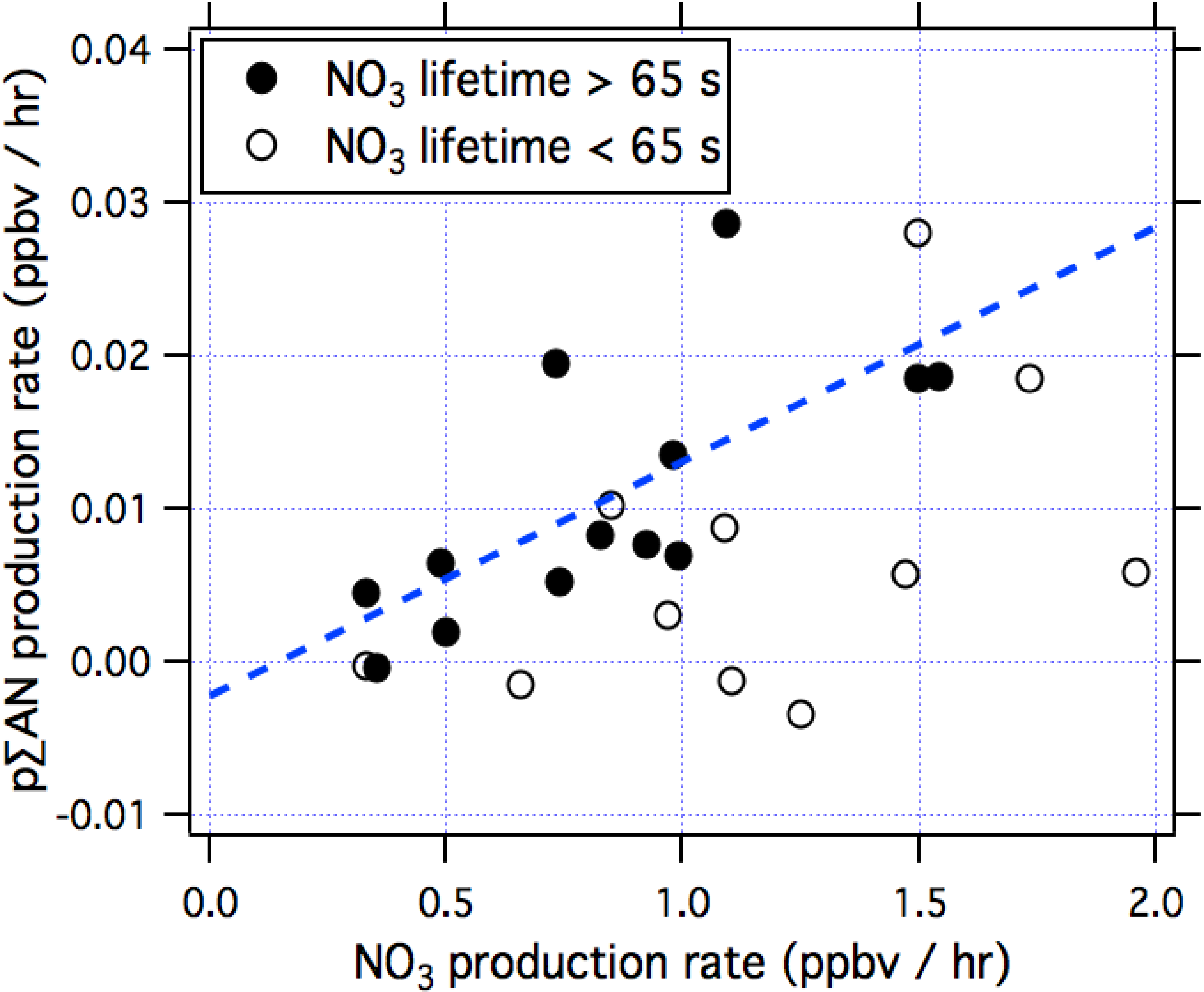
-ONO2 mass only.

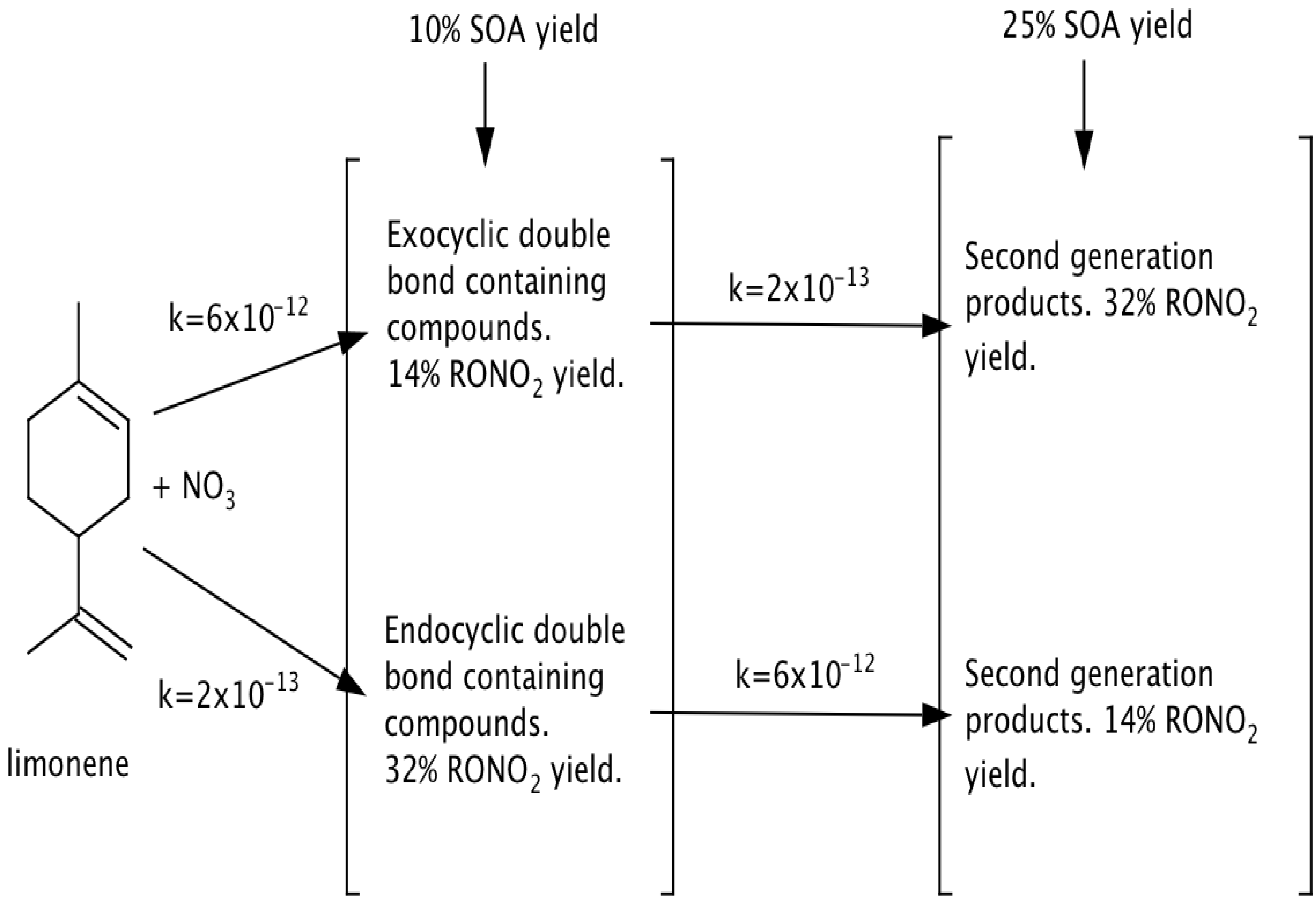
If mass of organic is 200-300 amu, then

27-40% of nighttime growth has an – ONO_2 functional group.

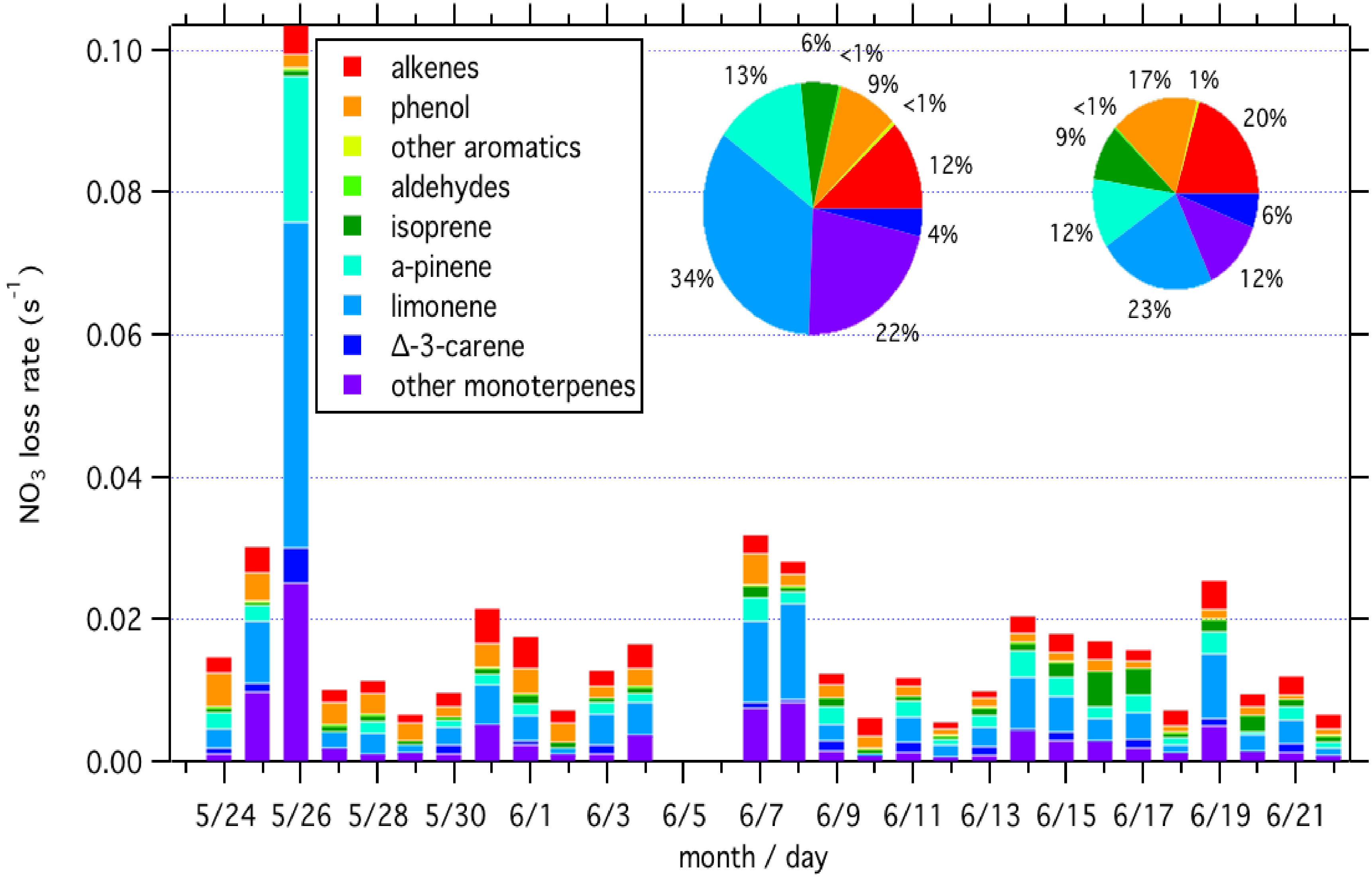
All of it—NO_3 chemistry??

What else can we learn about the molecules responsible for aerosol growth?

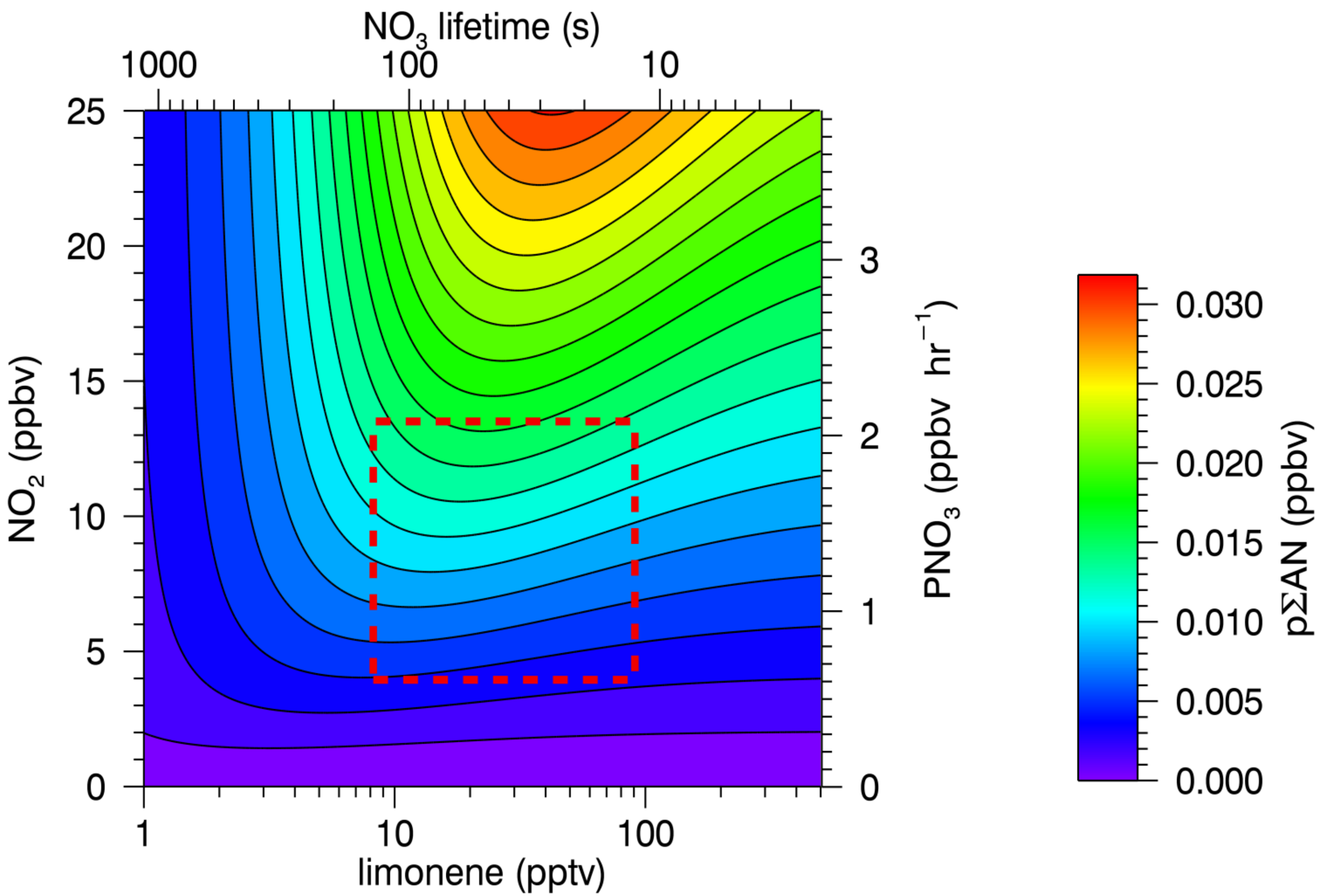

NO$_3$ lifetime > 65 s
NO$_3$ lifetime < 65 s
pΣAN production rate (ppbv / hr)
0.04
0.03
0.02
0.01
0.00
-0.01
0.0
0.5
1.0
1.5
2.0
NO$_3$ production rate (ppbv / hr)



10% SOA yield
25% SOA yield
k=6x10^-12
Exocyclic double bond containing compounds. 14% RONO2 yield.
k=2x10^-13
Second generation products. 32% RONO2 yield.
+ NO3
limonene
k=2x10^-13
Endocyclic double bond containing compounds. 32% RONO2 yield.
k=6x10^-12
Second generation products. 14% RONO2 yield.



alkenes
phenol
other aromatics
aldehydes
isoprene
a-pinene
limonene
Δ-3-carene
other monoterpenes
6%
<1%
13%
9%
<1%
12%
4%
34%
22%
17%
1%
<1%
20%
9%
6%
12%
12%
23%
0.10
0.08
0.06
0.04
0.02
0.00
NO3 loss rate (s-1)
5/24
5/26
5/28
5/30
6/1
6/3
6/5
6/7
6/9
6/11
6/13
6/15
6/17
6/19
6/21
month / day



NO3 lifetime (s)
1000
100
10
25
20
15
10
5
0
NO2 (ppbv)
1
10
100
limonene (pptv)
3
2
1
0
PNO3 (ppbv hr−1)
0.030
0.025
0.020
0.015
0.010
0.005
0.000
pΣAN (ppbv)

Aerosol Result #1

NO_3 radical chemistry is perhaps the primary source of organic aerosol in the SJV!

Result #1 continued

These results implying an NO_3 source for a major fraction of organic aerosol in the SJV indicate that the chemical composition of the aerosol and perhaps the time of day of its production should have changed dramatically over the last decade.

It's possible that the same source molecules oxidized by other pathways give identical aerosol yields. But if not, the amount of secondary organic aerosol should have undergone measureable changes in response to the NOx decreases over the last decade.

Policy Relevant Conclusion

NO_x reductions may have a substantial secondary organic aerosol cobenefit in the SJV. This is in addition to the benefits for ozone and for wintertime inorganic aerosol.

Summary

Two threads of analysis of SJV observations connecting nitrogen oxides to O_3 and to fine particles.

There are lots and lots of things to think about in this data set. Allen Goldstein will show you some more of them after lunch.

Thank you