$RONO_2$ in the LA Basin

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Photo Credit: H. Fuelberg

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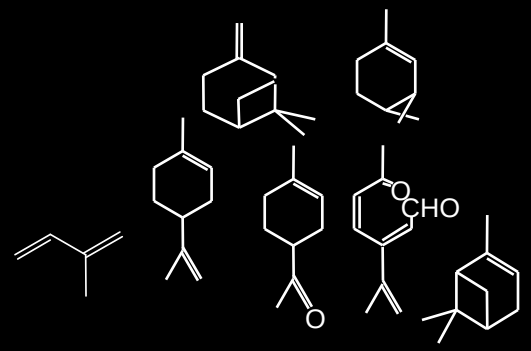
NASA ESE Fellowship

In July Postdoc with David Fahey: NOAA

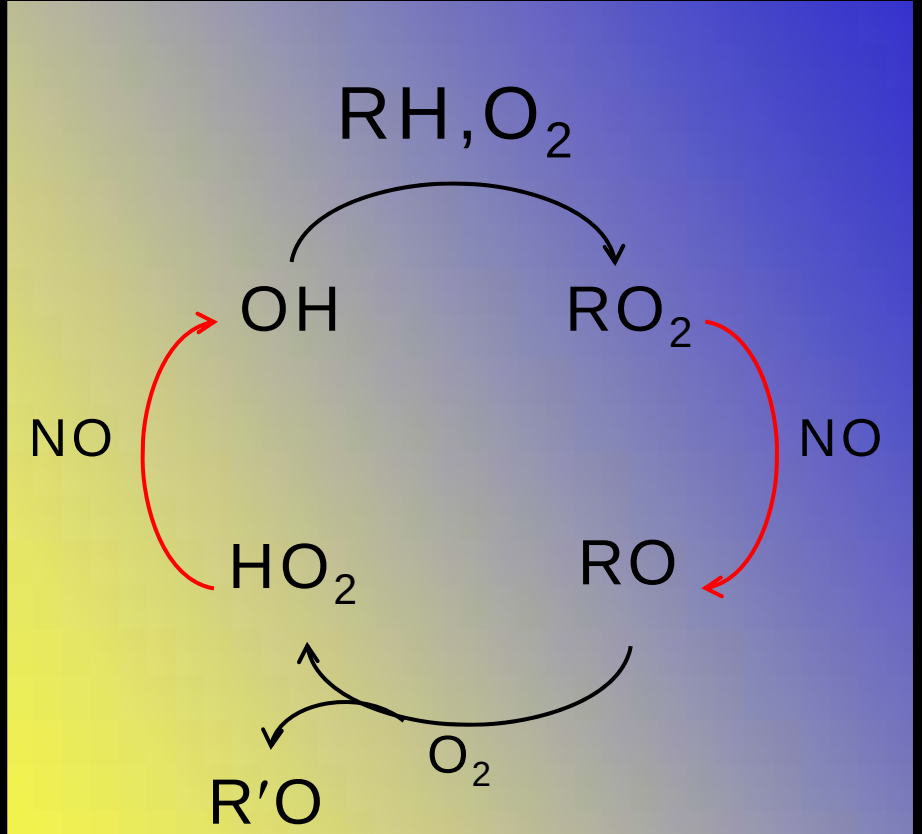
Photochemical ozone production:

HO_x radical chain reactions propagate at rates set by the mix of NO_x ($NO+NO_2$) and gas phase organics

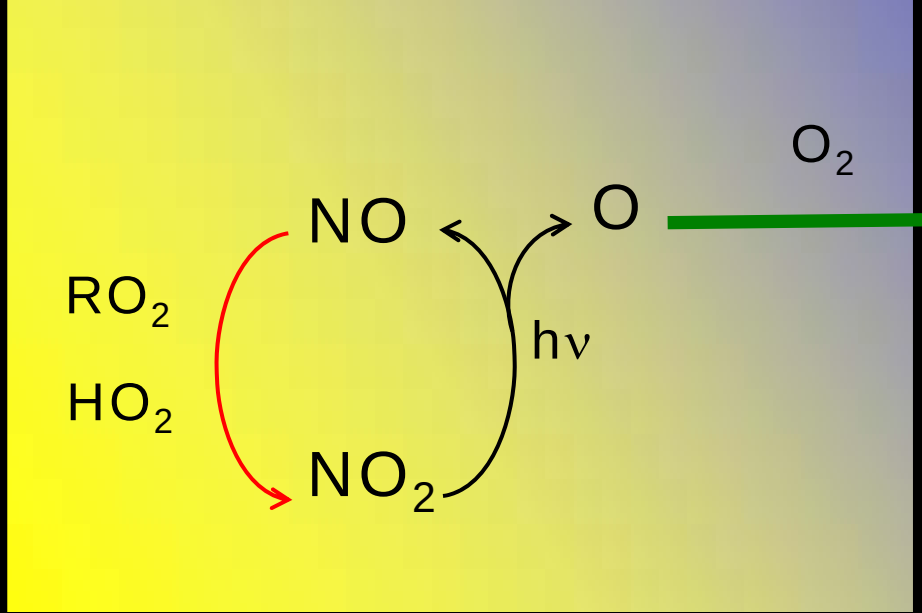
HO_x + NO_x +



HO_x Cycle



NO_x Cycle



O_3

NO_x vs. VOC limited: NO_x and HO_x radicals

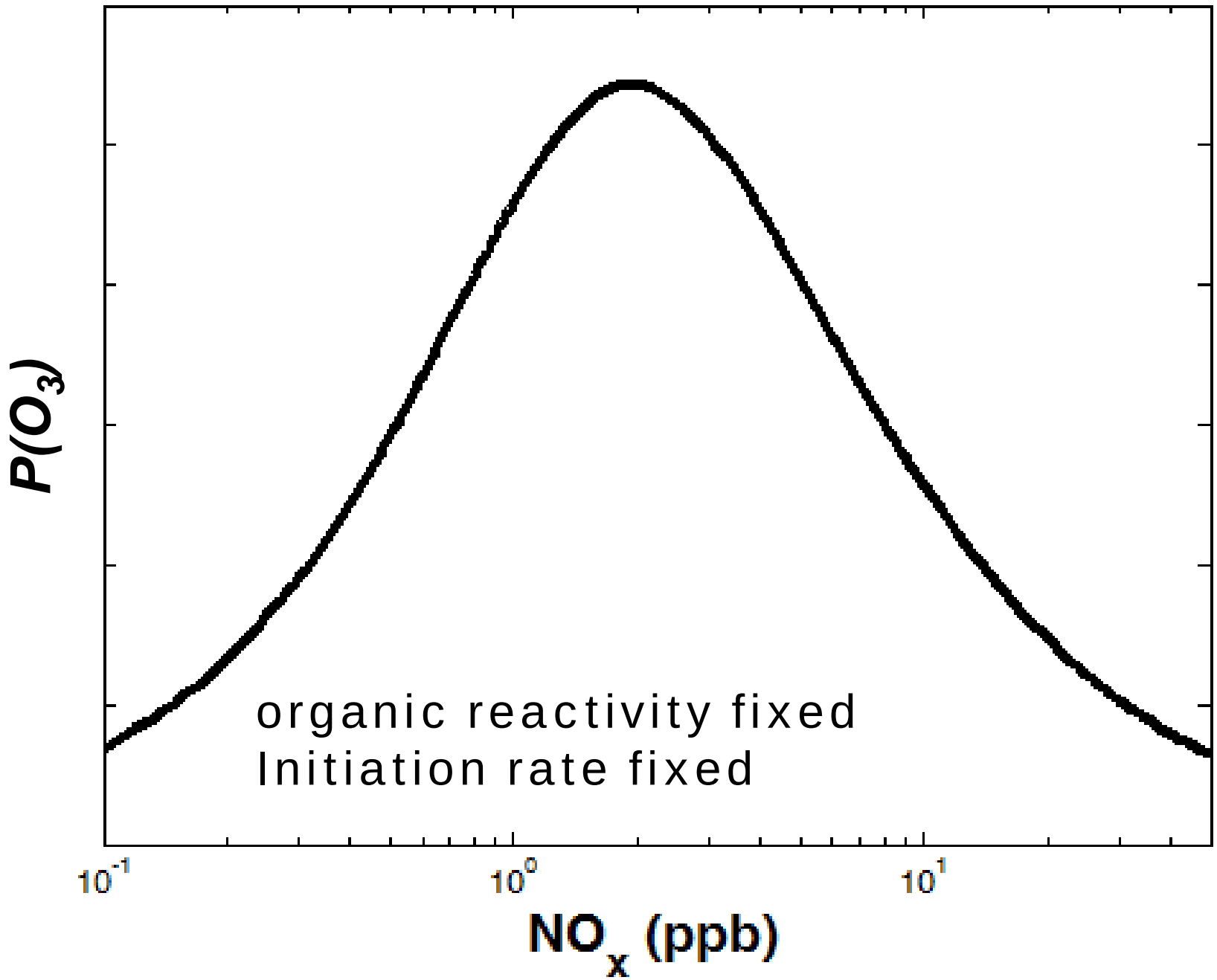
VOC Limited

$OH + NO_2$ faster than $OH + VOC$

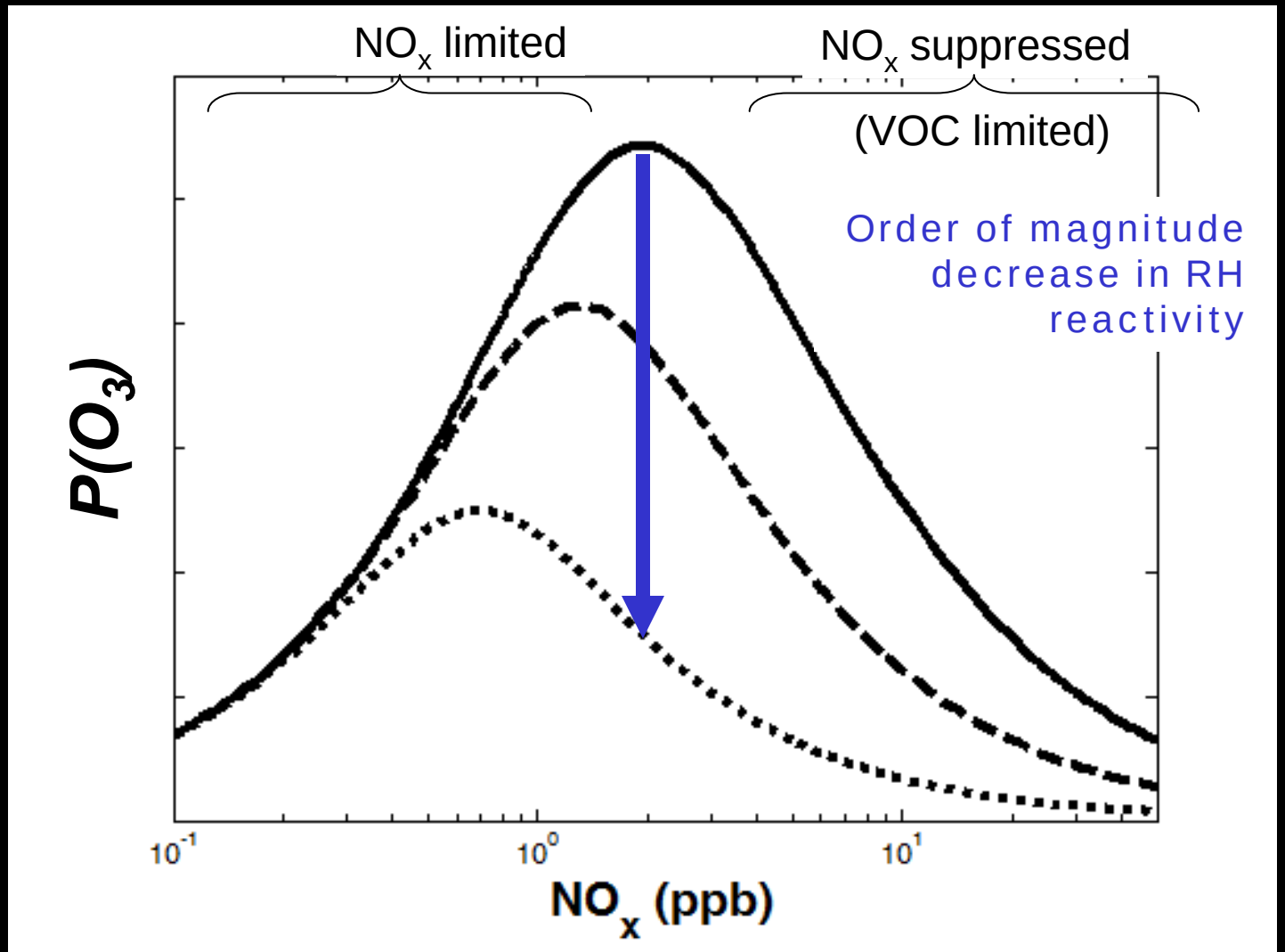
NO_x limited

$HO_2 + RO_2$ primary sink of HO_x

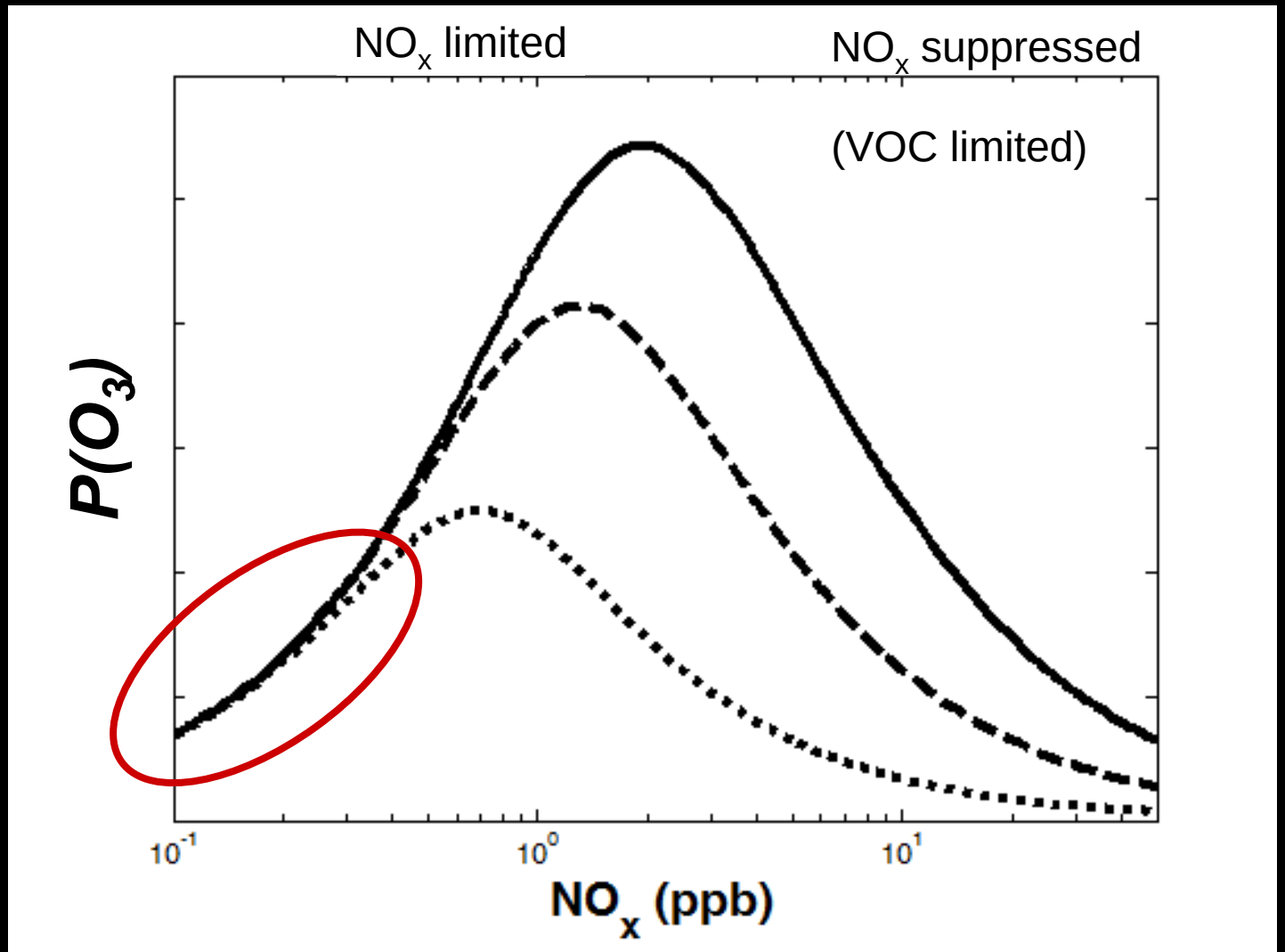
$NO + HO_2/RO_2$ enhances OH without affecting HO_2/RO_2


P(O3)
organic reactivity fixed
Initiation rate fixed
10-1
100
101
NOx (ppb)

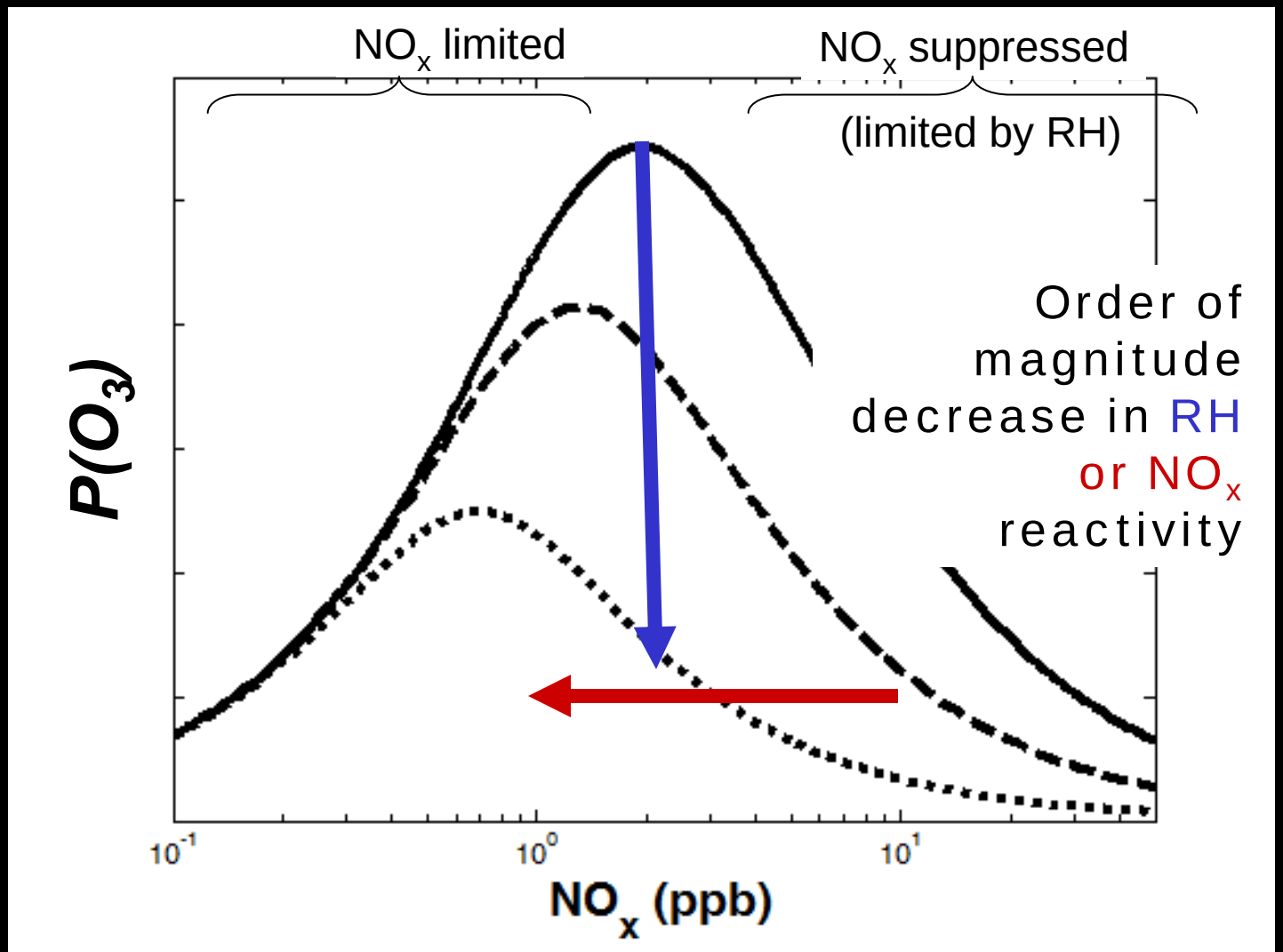
Vary organic reactivity



At low NO_x, organic reductions have zero direct effect



At high NO_x, reducing organics is presumed effective at reducing the rate of ozone production: Los Angeles



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

$$NO_2 + OH \xrightarrow{M} HNO_3$$
$$RO_2 + NO \xrightarrow{M} RONO_2$$

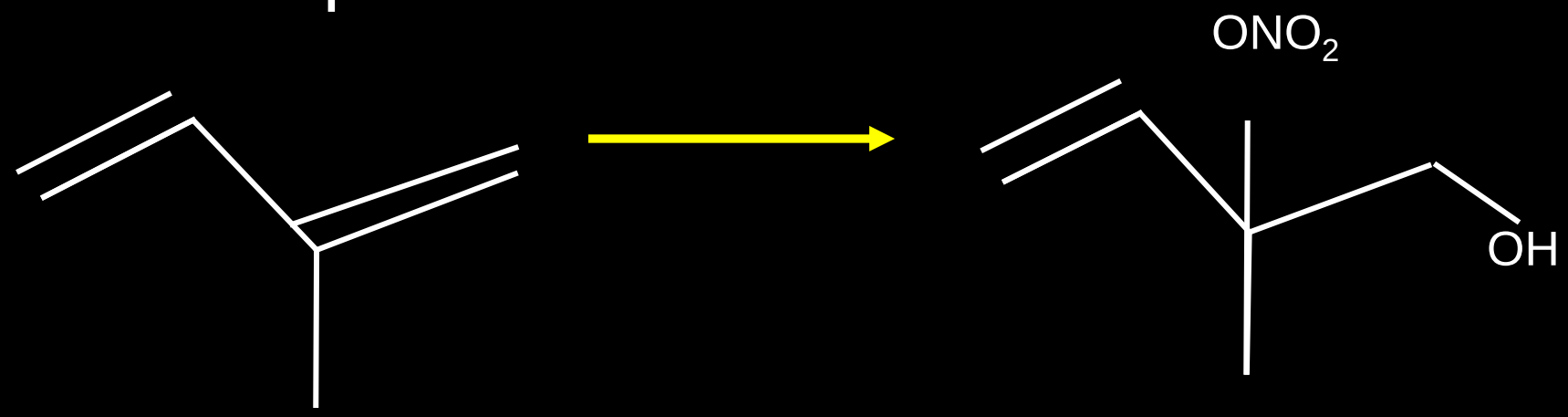
$$RO_2 + NO \longrightarrow RO + NO_2 \qquad 1-\alpha$$

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

We expect dozens to hundreds of $RONO_2$ compounds, few of which have been synthesized, characterized or observed specifically in the atmosphere.

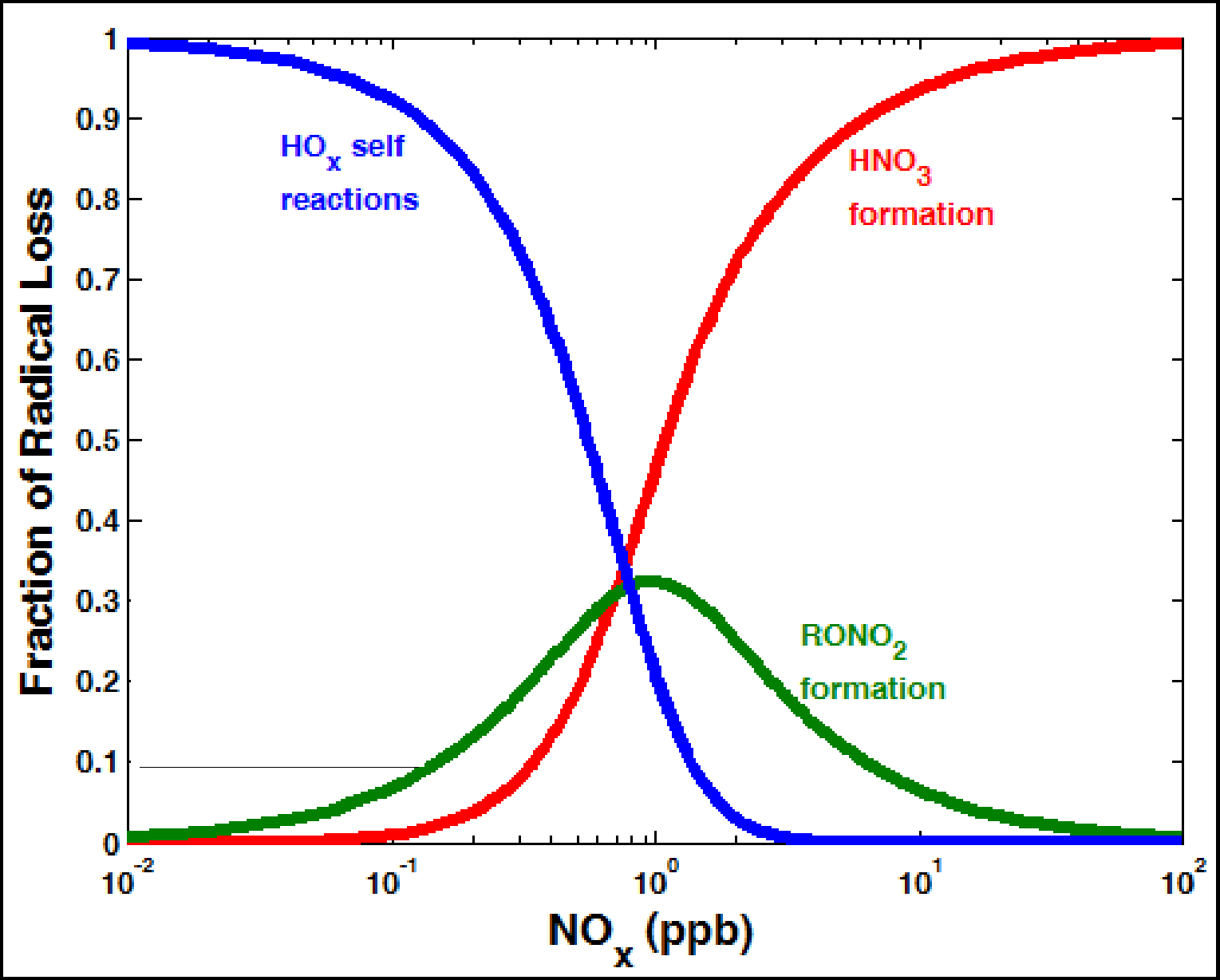
Multifunctional $RONO_2$

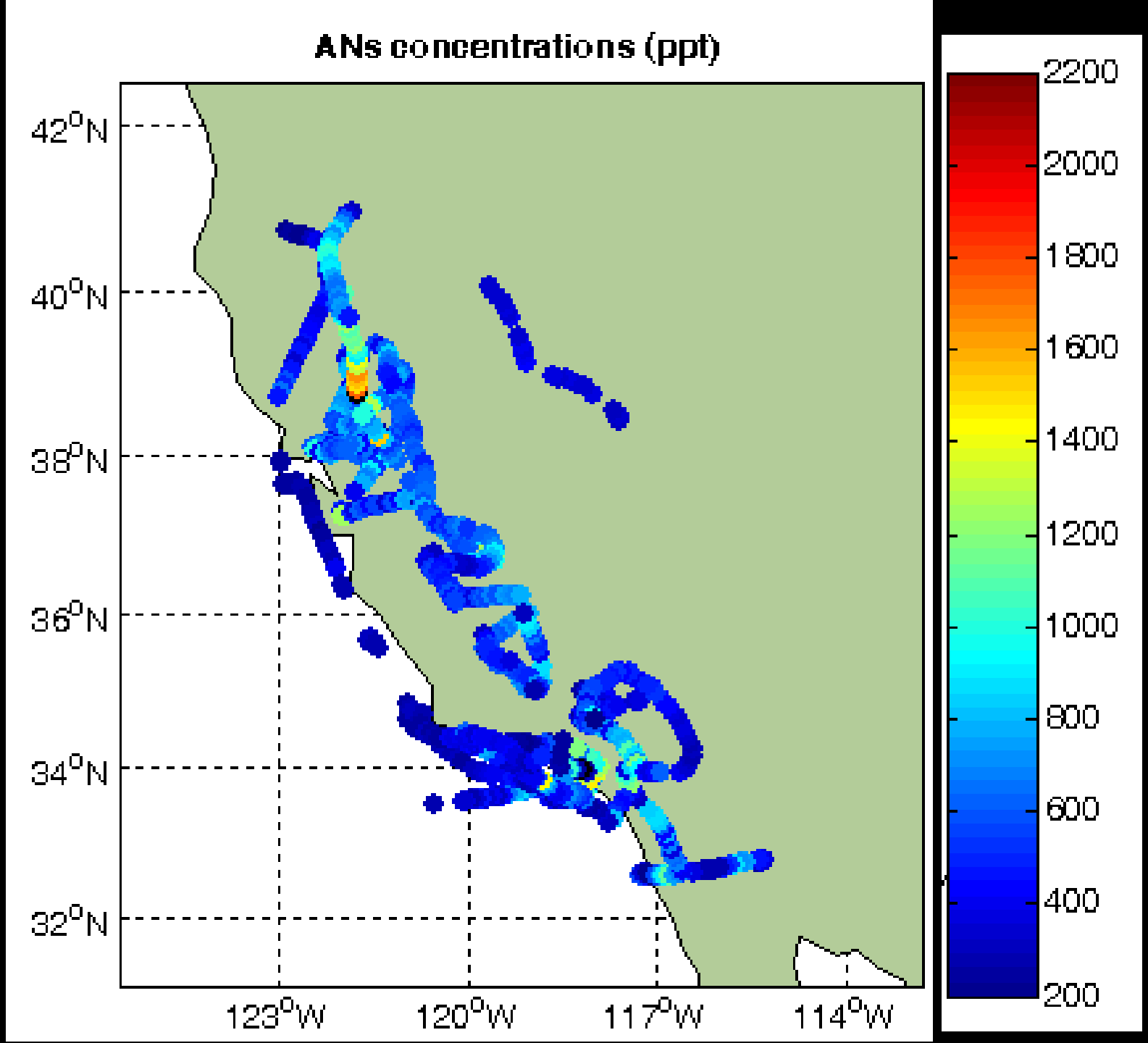
For example:

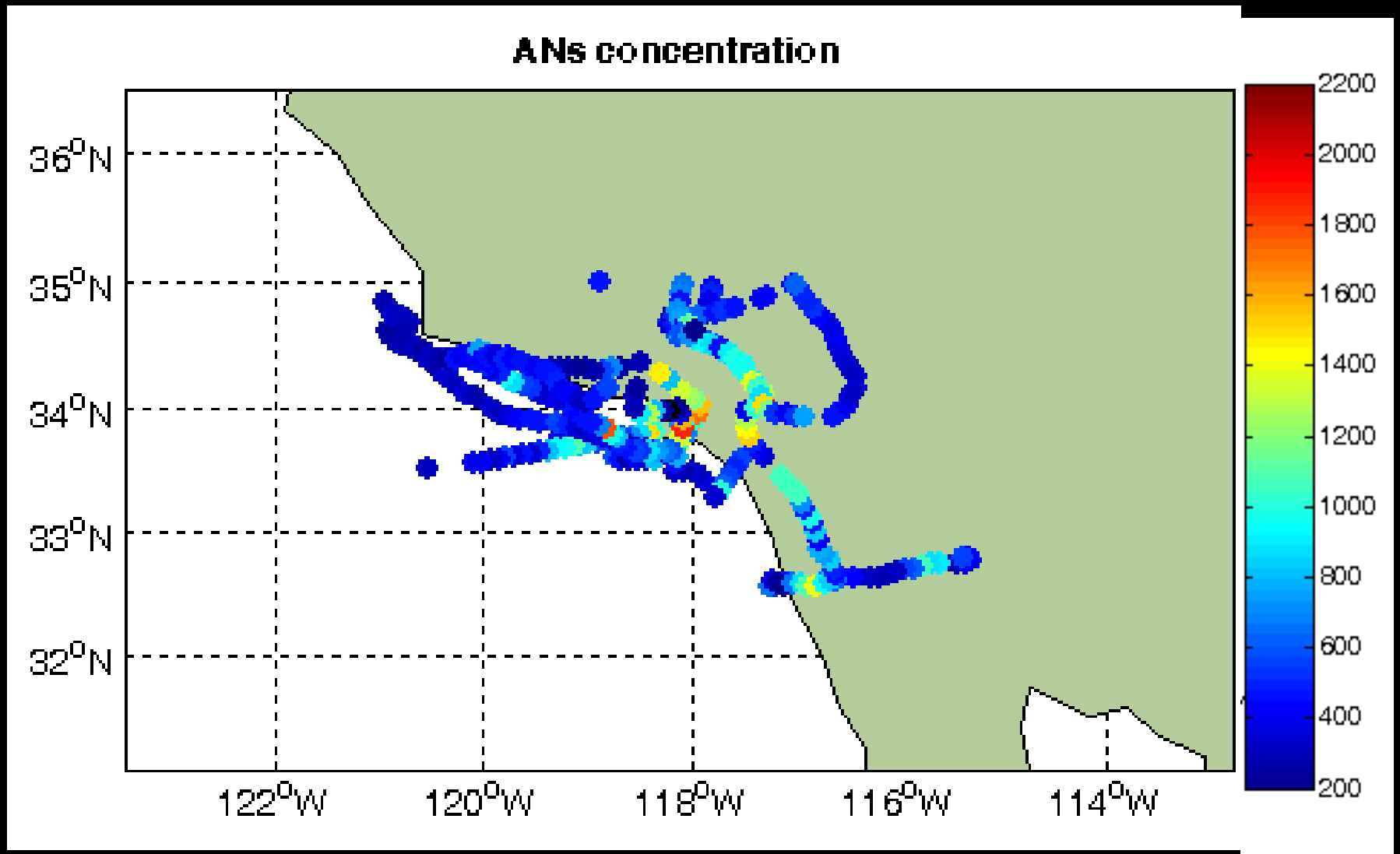


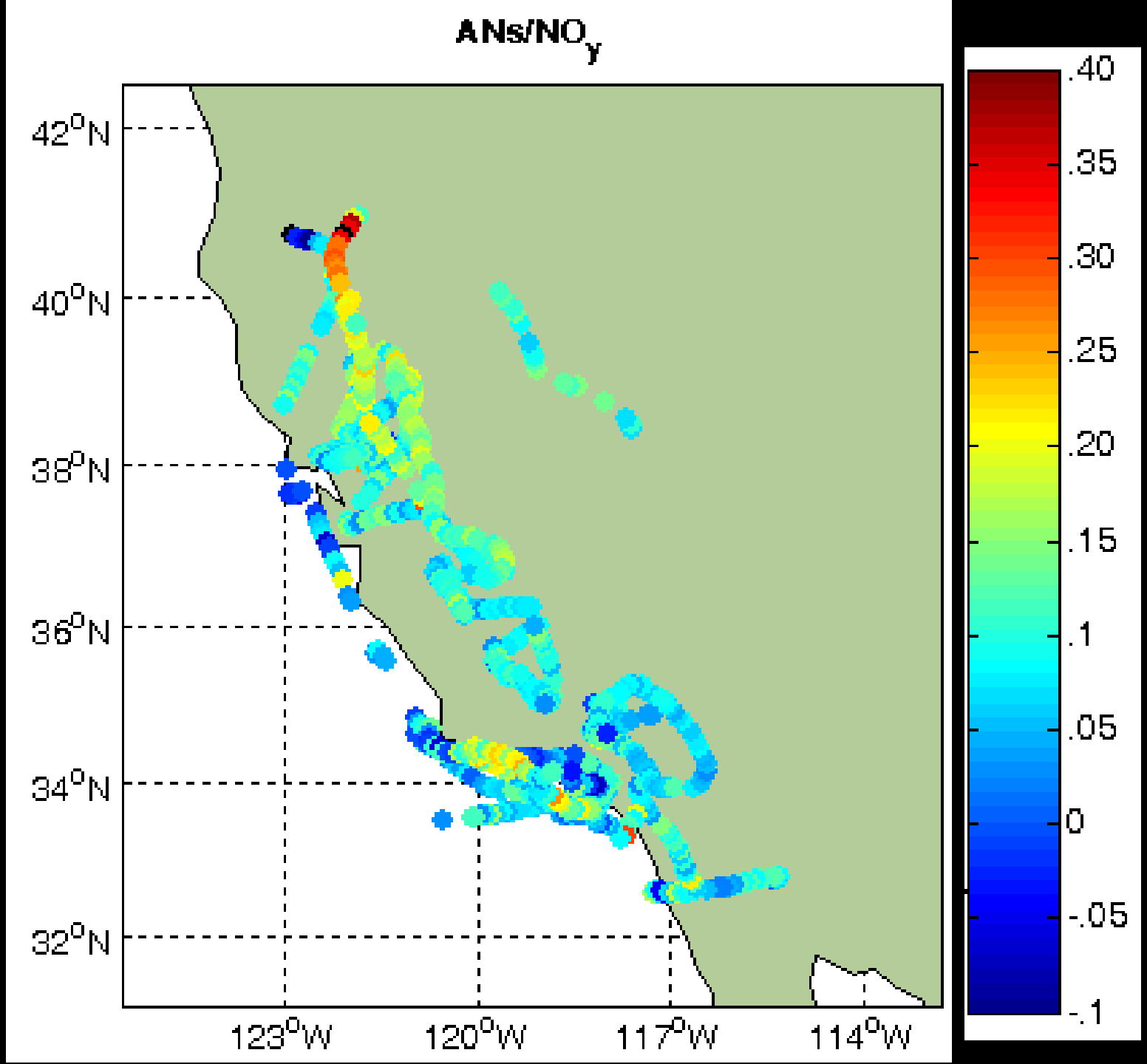
Toluene → Toluene-hydroxynitrate

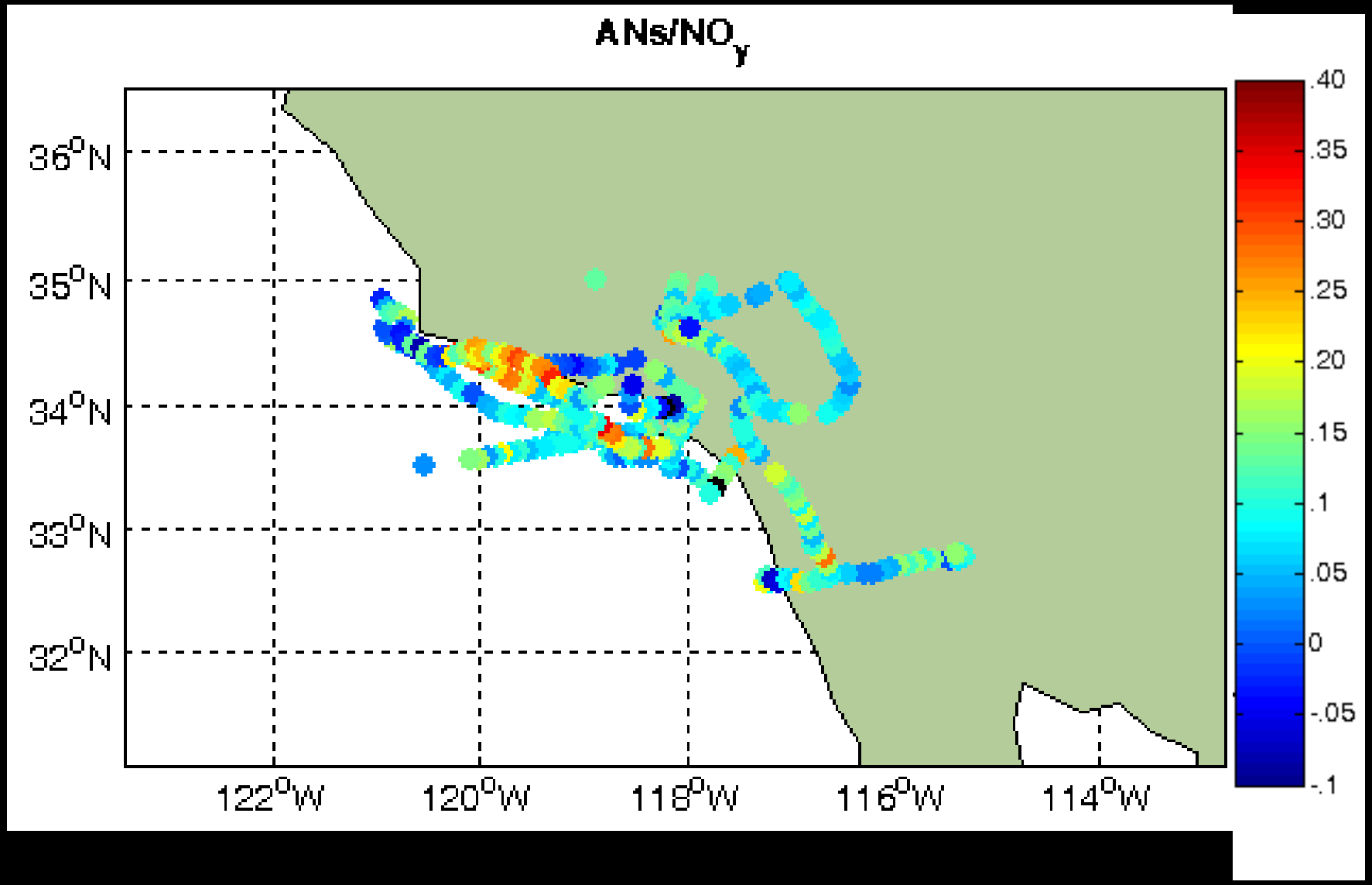
HO_x Chain termination

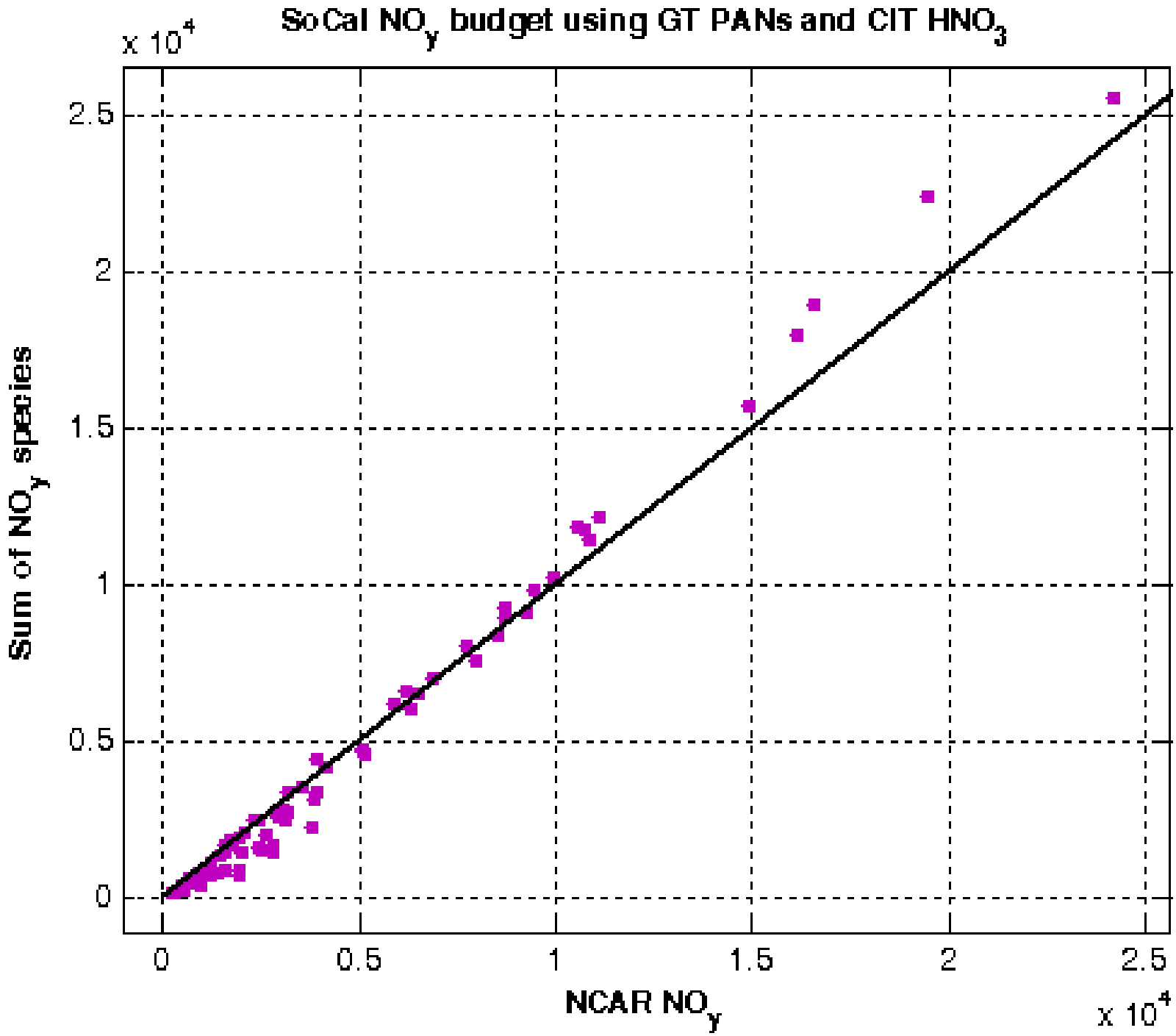


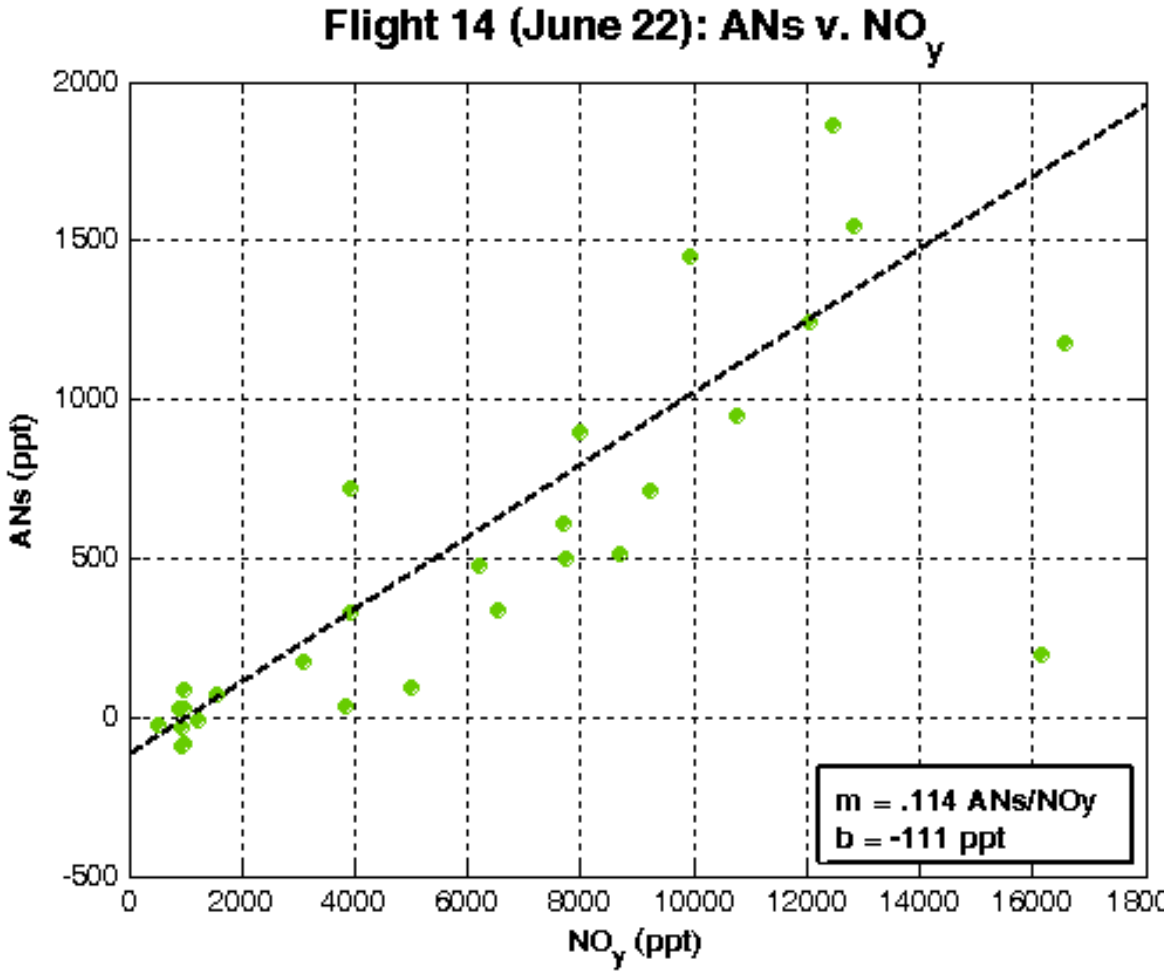

ANs concentrations (ppt)
42°N
40°N
38°N
36°N
34°N
32°N
123°W
120°W
117°W
114°W
2200
2000
1800
1600
1400
1200
1000
800
600
400
200

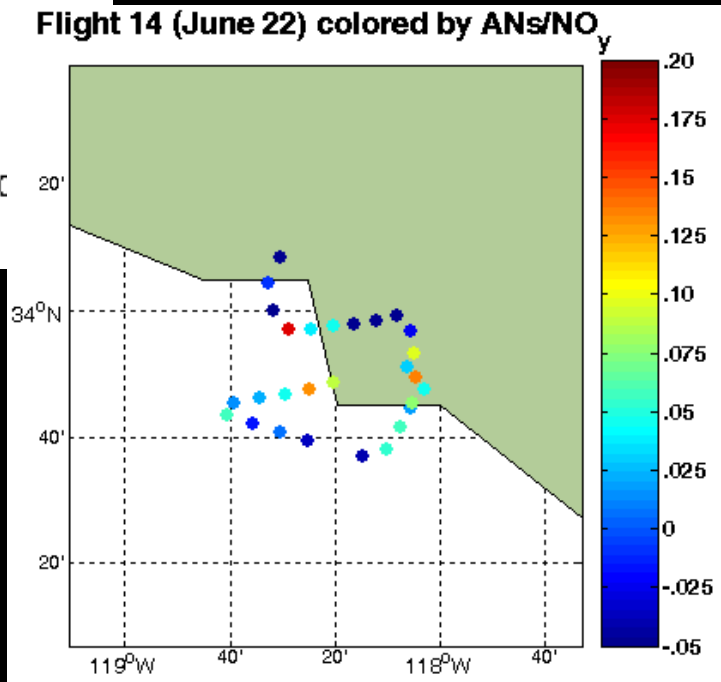

ANs concentration
36°N
35°N
34°N
33°N
32°N
122°W
120°W
118°W
116°W
114°W
2200
2000
1800
1600
1400
1200
1000
800
600
400
200


ANs/NO$_y$
42°N
40°N
38°N
36°N
34°N
32°N
123°W
120°W
117°W
114°W
.40
.35
.30
.25
.20
.15
.1
.05
0
-.05
-.1

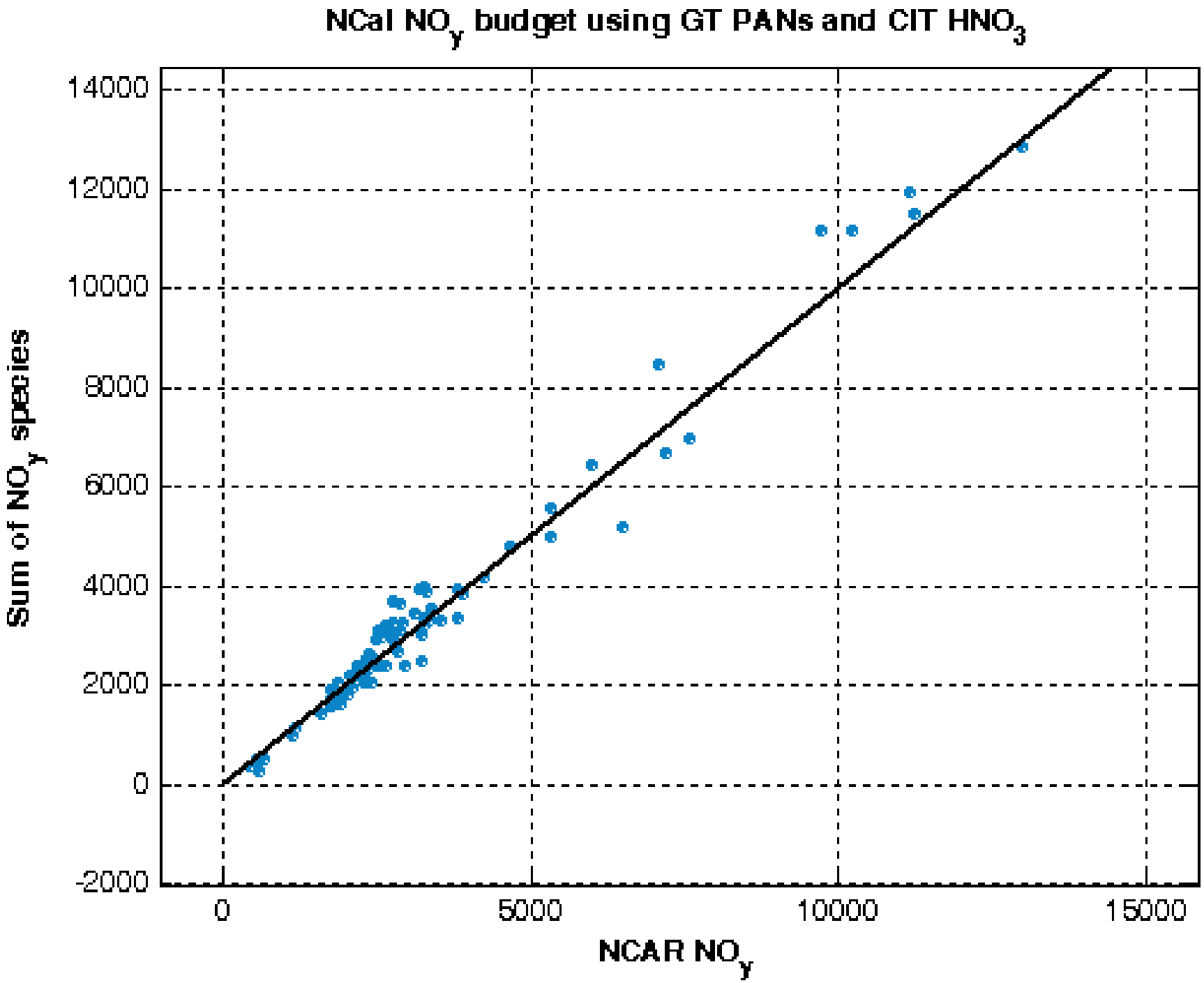

ANs/NO$_y$
36°N
35°N
34°N
33°N
32°N
122°W
120°W
118°W
116°W
114°W
.40
.35
.30
.25
.20
.15
.1
.05
0
-.05
-.1

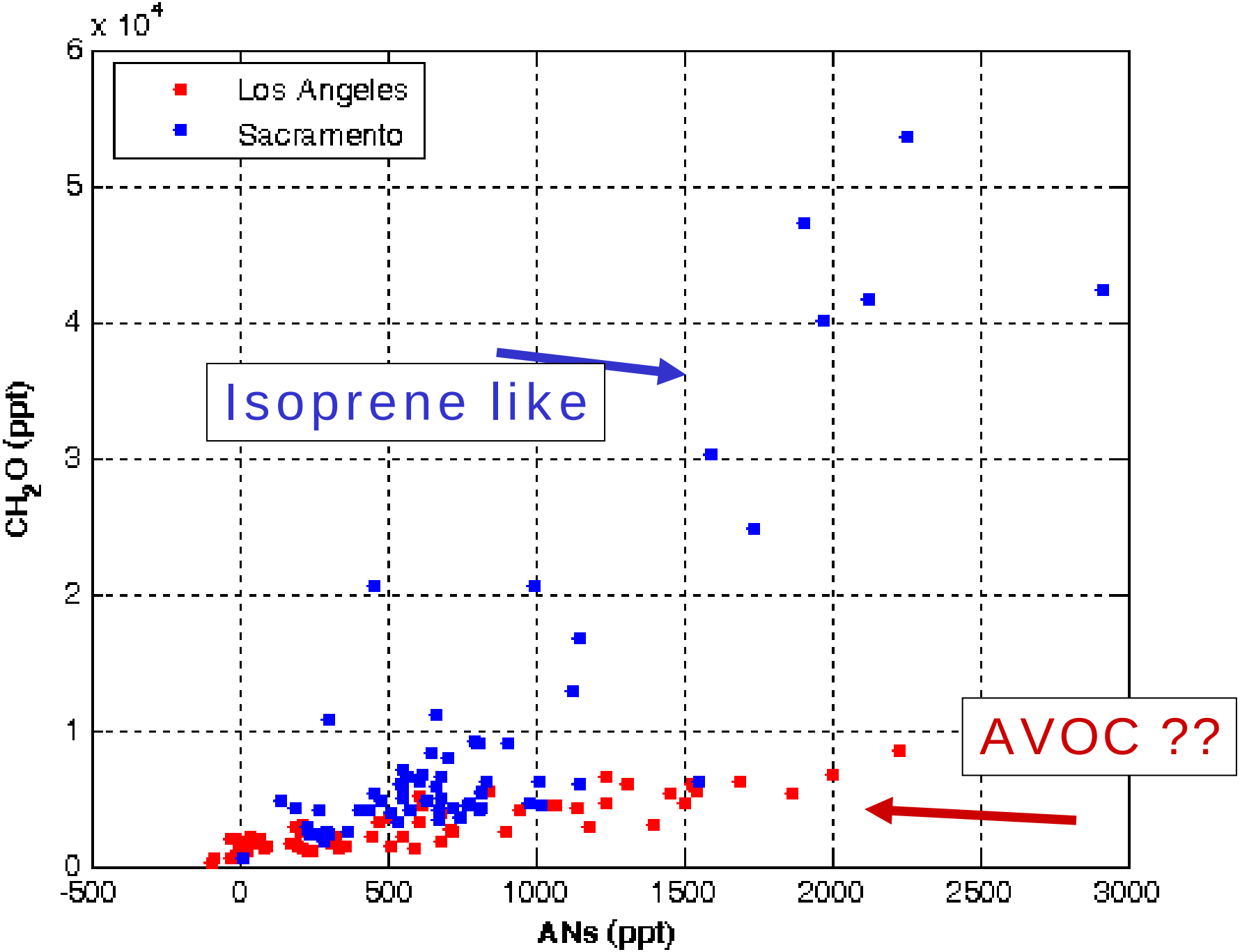

SoCal NOy budget using GT PANs and CIT HNO3
x 10^4
2.5
2
1.5
1
0.5
0
Sum of NOy species
0
0.5
1
1.5
2
2.5
NCAR NOy
x 10^4





ΣANs~11% of NO_y


NCal NOy budget using GT PANs and CIT HNO3
Sum of NOy species
NCAR NOy
14000
12000
10000
8000
6000
4000
2000
0
-2000
0
5000
10000
15000


x 10^4
6
5
4
3
2
1
0
-500
0
500
1000
1500
2000
2500
3000
Los Angeles
Sacramento
Isoprene like
AVOC ??
CH2O (ppt)
ANs (ppt)

$\Delta O_x / \Delta \Sigma RONO_2 = 2(1-\alpha)/\alpha$

$$RH + OH \rightarrow RO_2$$

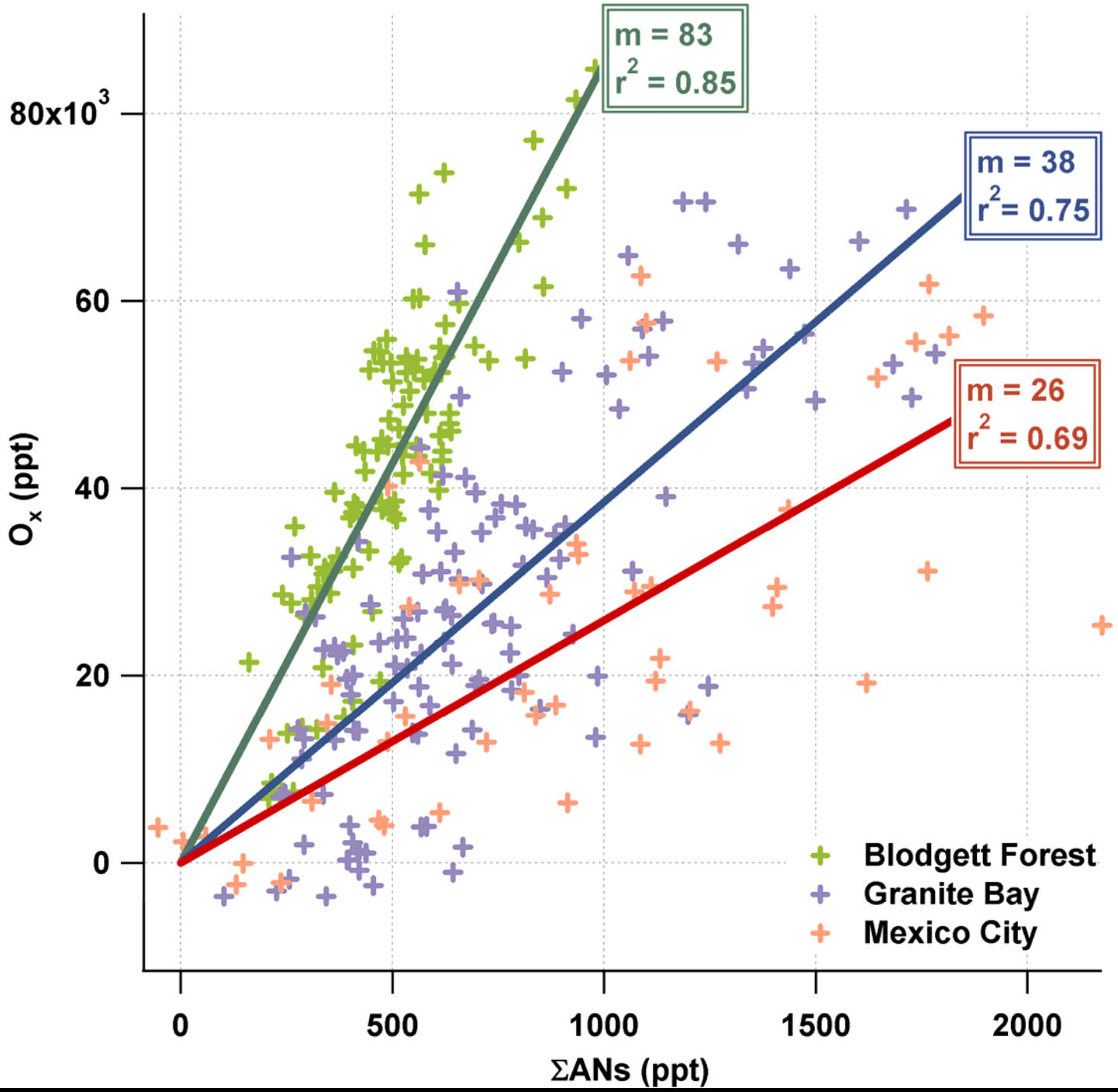
$$RO_2 + NO \rightarrow \alpha RONO_2 + (1-\alpha)(RO^{\cdot} + NO_2)$$

$$RO^{\cdot} + O_2 \rightarrow HO_2 + R'O$$

$$HO_2 + NO \rightarrow OH + NO_2$$

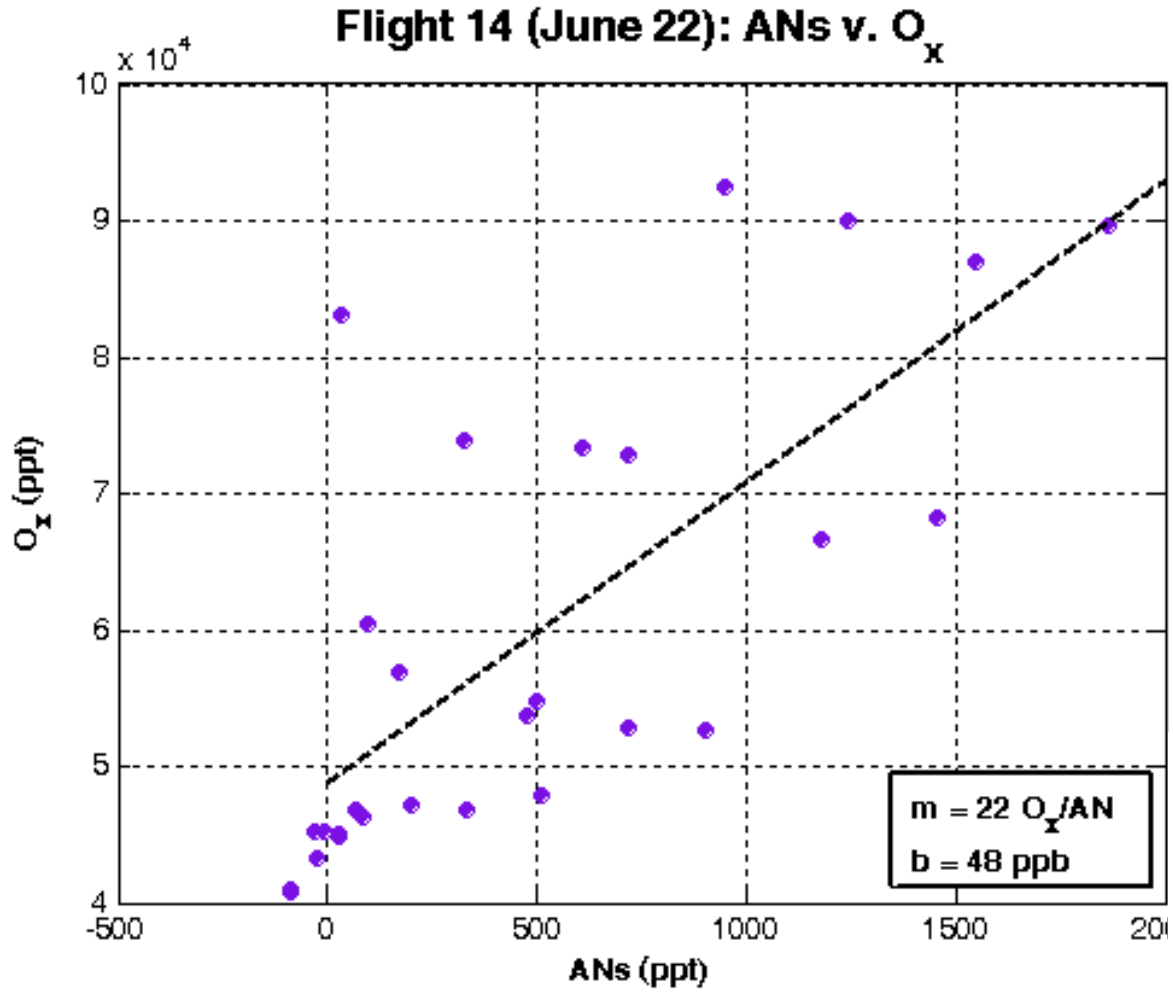
$$2NO_2 \rightarrow 2O_3$$

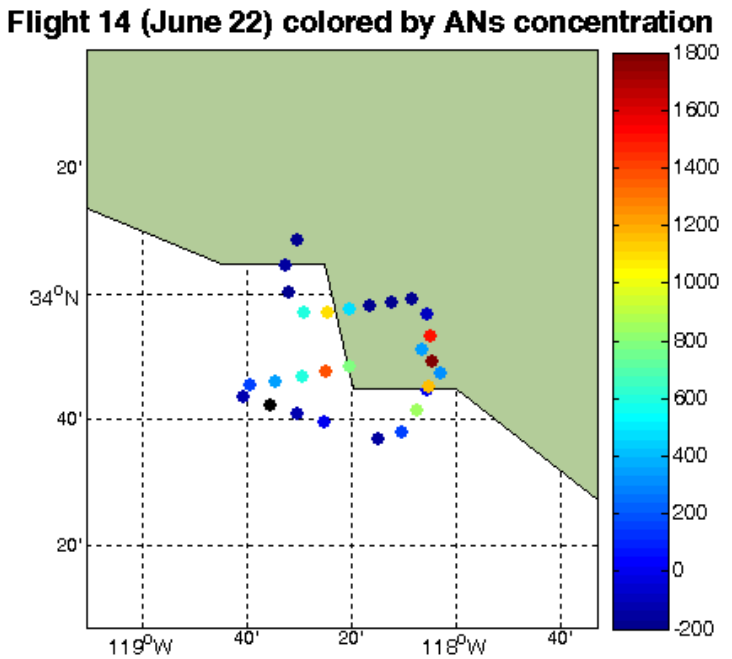
$$RH \rightarrow \alpha RONO_2 + 2(1-\alpha)O_3 + R'O$$


m = 83
r2 = 0.85
m = 38
r2 = 0.75
m = 26
r2 = 0.69
80x103
60
40
20
0
Ox (ppt)
0
500
1000
1500
2000
ΣANs (ppt)
Blodgett Forest
Granite Bay
Mexico City

Higher yield of $RONO_2$ in Mexico City than any other place we've studied

	Location	O_x / $\Sigma RONO_2$	Effective α
Urban	Mexico City	26	7.1%
	Houston	35	5.4%
	Sacramento	37	5.1%
Non-urban	Southeast US	59	3.3%
	Big Hill	51	3.8%
	Blodgett Forest	63	3.1%

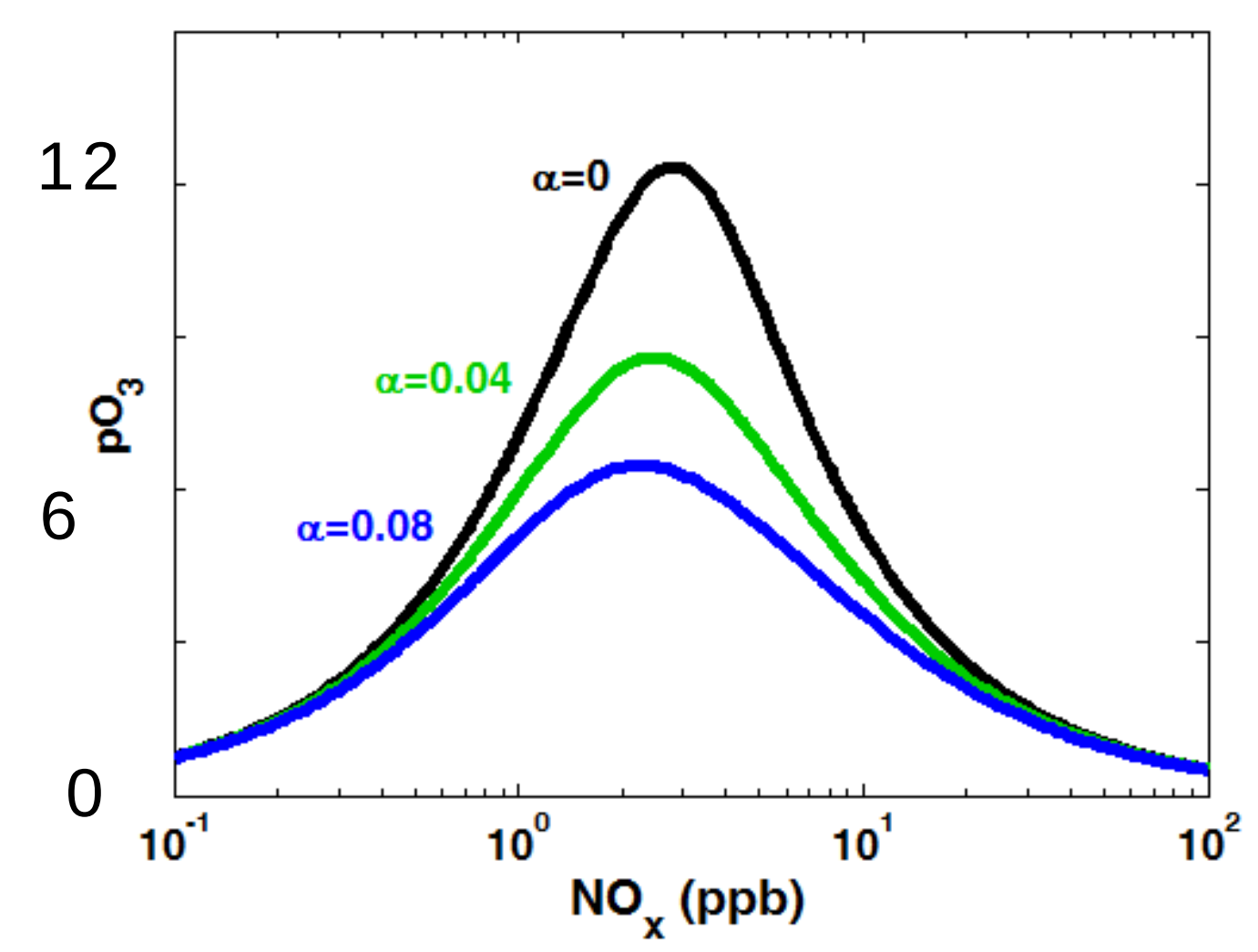

Flight 14 (June 22): ANs v. O_x
x 10^4
O_x (ppt)
ANs (ppt)
m = 22 O_x/AN
b = 48 ppb


Flight 14 (June 22) colored by ANs concentration
34°N
119°W
118°W

$\alpha \sim 8.3\%$

Implications:

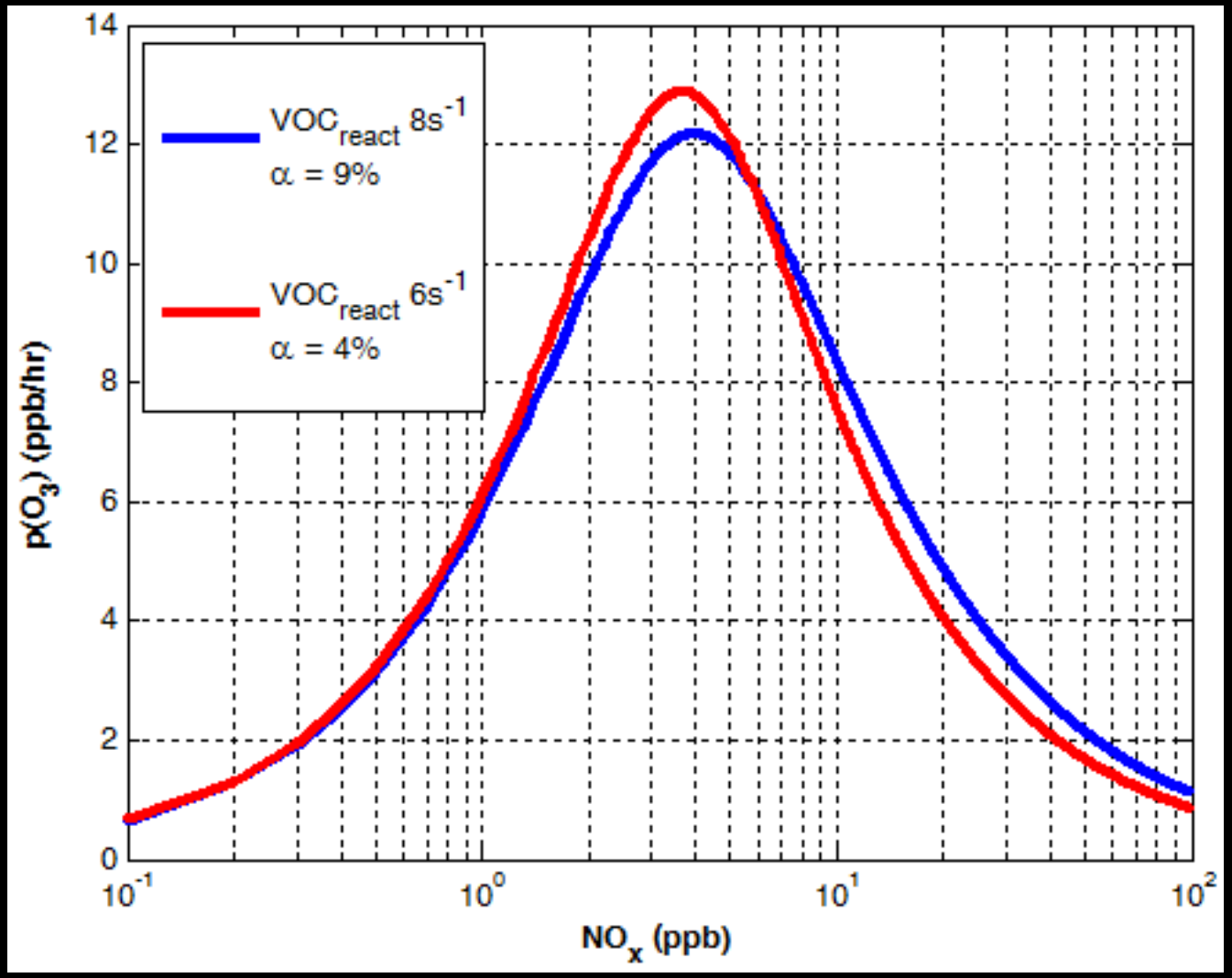
Ozone production and α



What if changes in VOC change α?

Selective reduction of long-chain VOC? Or of low vapor pressure VOC?

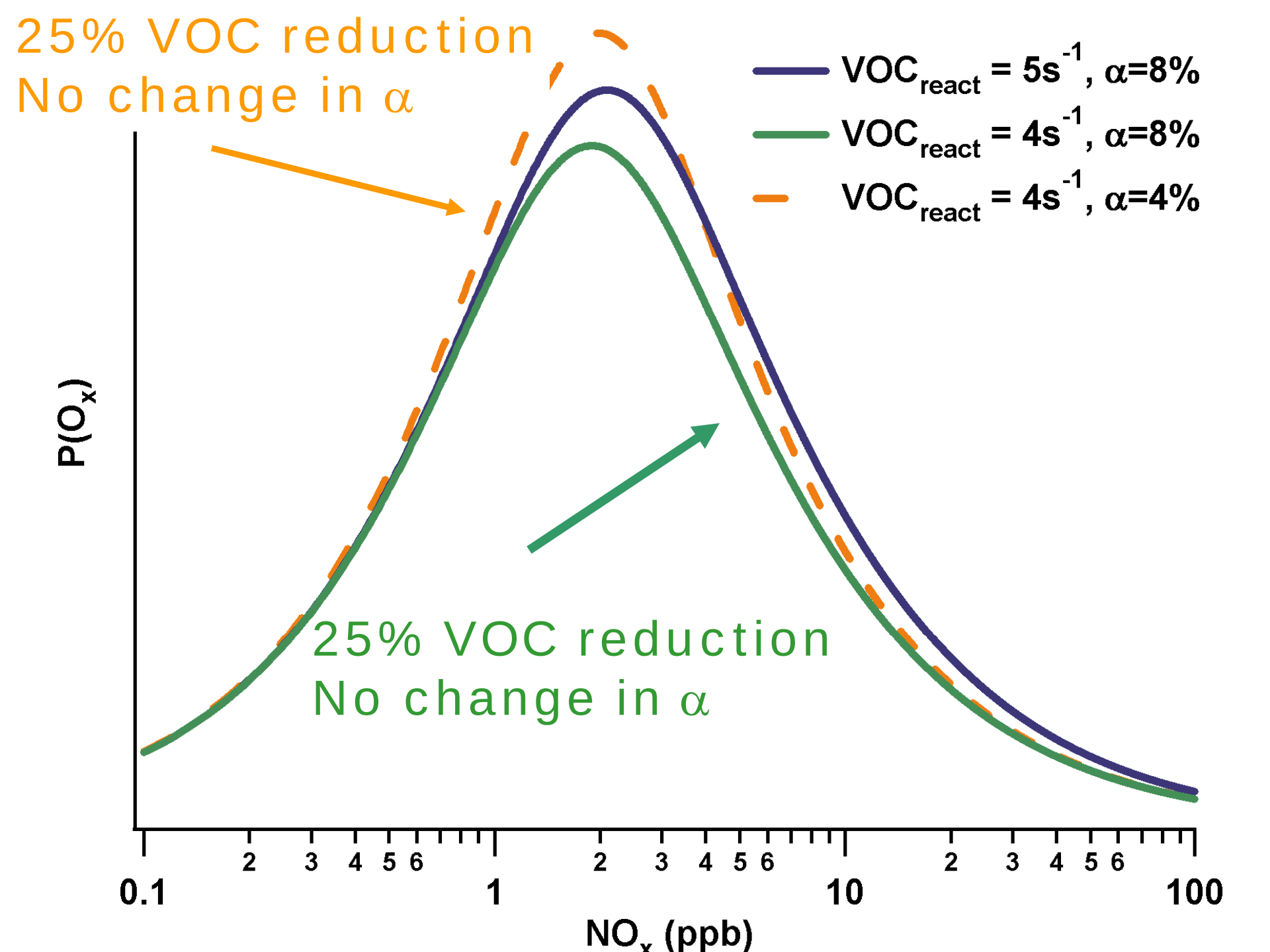
Selective reduction of high nitrate branching ratio VOC will increase $P(O_3)$



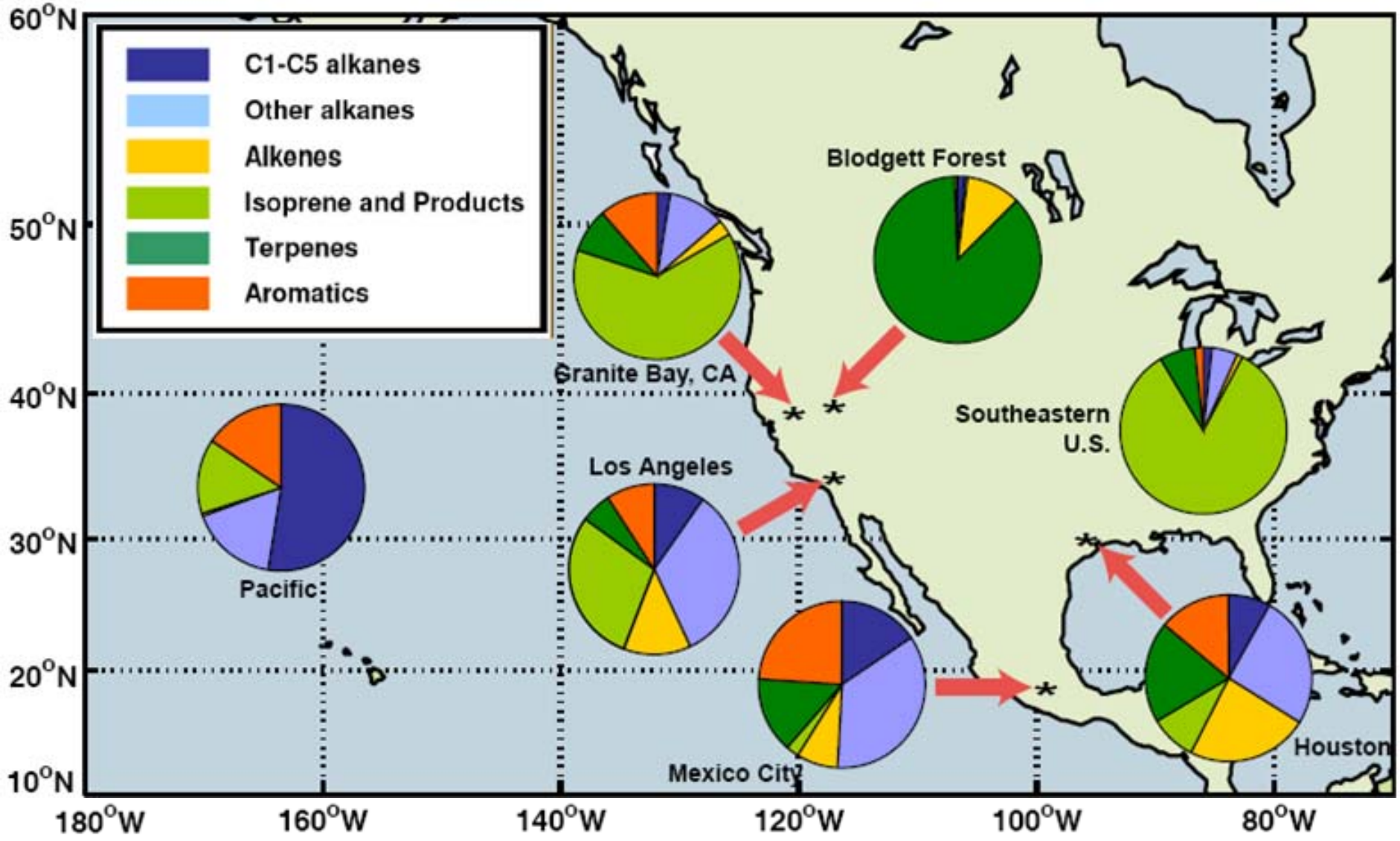
Here a 25% VOC reduction under

"VOC limited conditions"

increases O_3


25% VOC reduction
No change in α
VOC$_{react}$ = 5s^{-1}, α=8%
VOC$_{react}$ = 4s^{-1}, α=8%
VOC$_{react}$ = 4s^{-1}, α=4%
P(O$_x$)
25% VOC reduction
No change in α
0.1
1
10
100
2 3 4 5 6
NO$_x$ (ppb)

Sources of $RONO_2$:


C1-C5 alkanes
Other alkanes
Alkenes
Isoprene and Products
Terpenes
Aromatics
Blodgett Forest
Granite Bay, CA
Southeastern U.S.
Los Angeles
Pacific
Mexico City
Houston
60°N
50°N
40°N
30°N
20°N
10°N
180°W
160°W
140°W
120°W
100°W
80°W

Conclusions

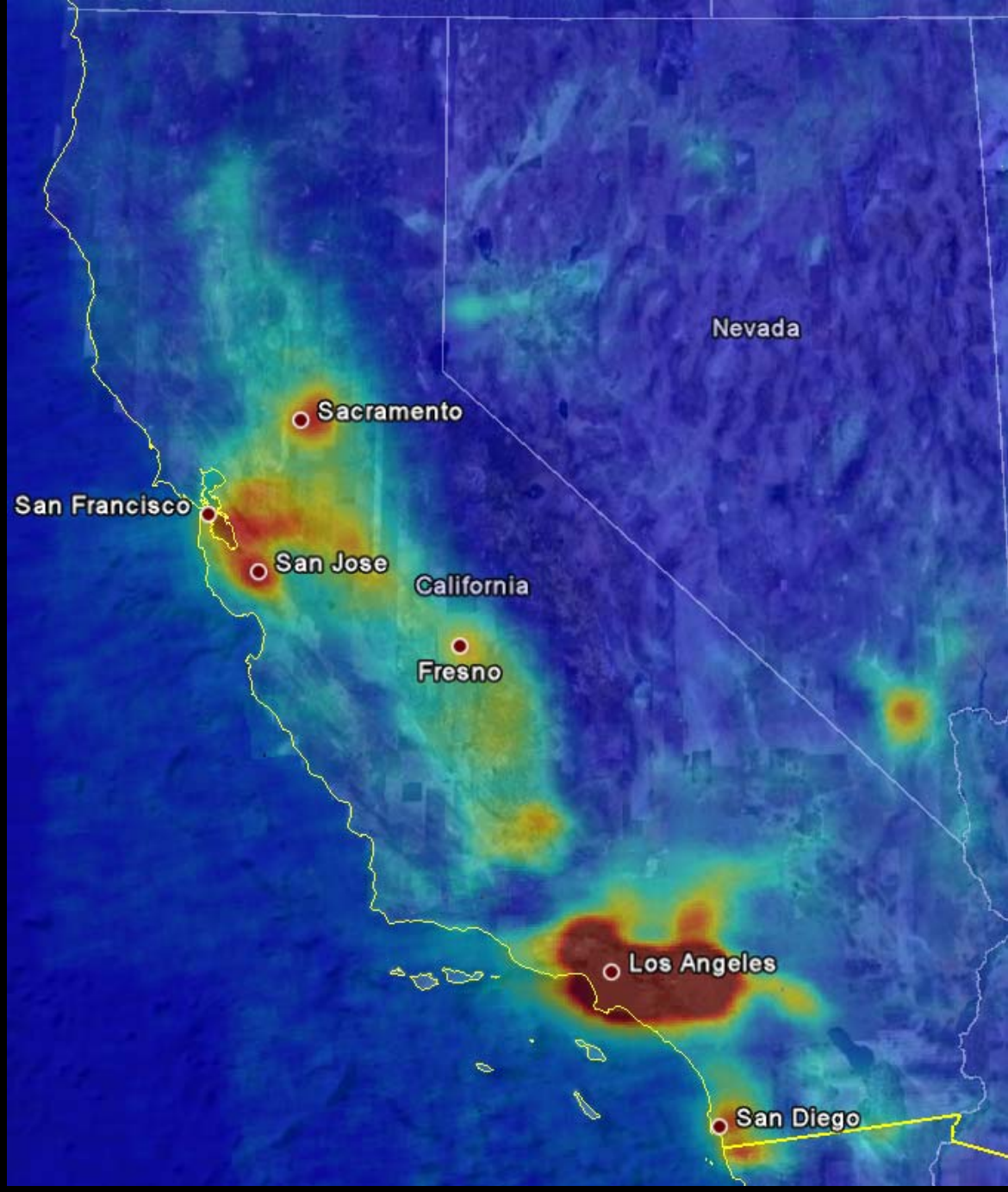
Changes in $RONO_2$ formation can reduce the effectiveness of VOC reductions for controlling urban O_3.

Questions:

Is this why (or part of the reason) O_x reductions are slowing?

How has $RONO_2$ formation (sources) changed over time in SCAQMD?

Thank you!


Nevada
Sacramento
San Francisco
San Jose
California
Fresno
Los Angeles
San Diego