# SEAC$^4$Rs Isoprene chemistry

SEAC4Rs Science Team Meeting

4/17/2014

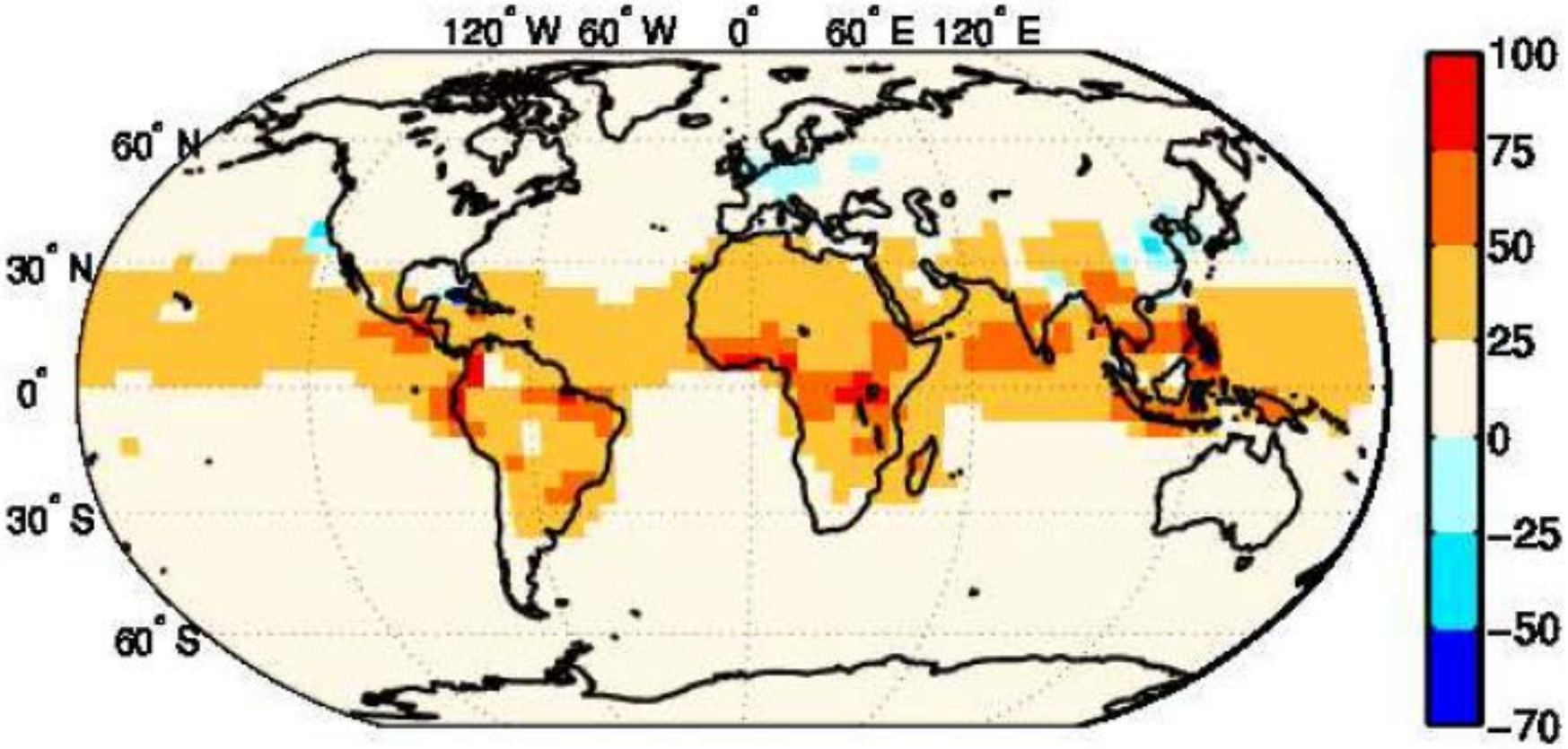
John Crounse, Paul Wennberg, Jason St. Clair, Alex Teng and SEAC4Rs science team

Caltech, Pasadena CA

# Big picture science question

- How will the impact of biogenic emissions on tropospheric ozone and organic aerosol change as anthropogenic emissions change?

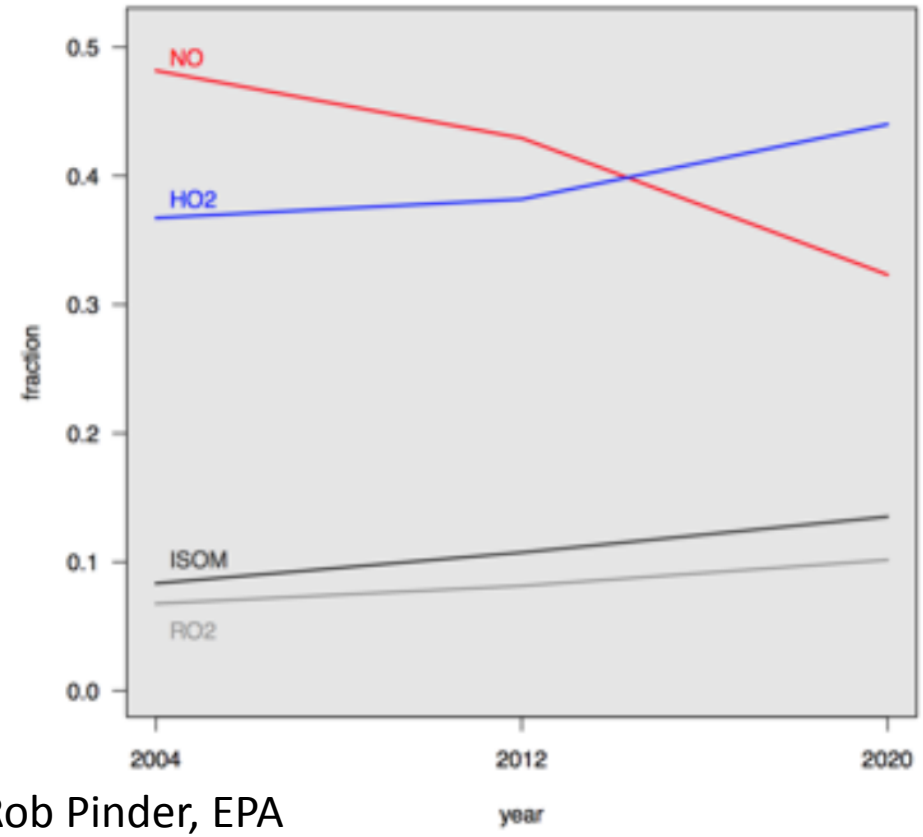
Percent change in tropospheric ozone column if all humans emitted $NO_x$ ($NO+NO_2$) like North Americans.



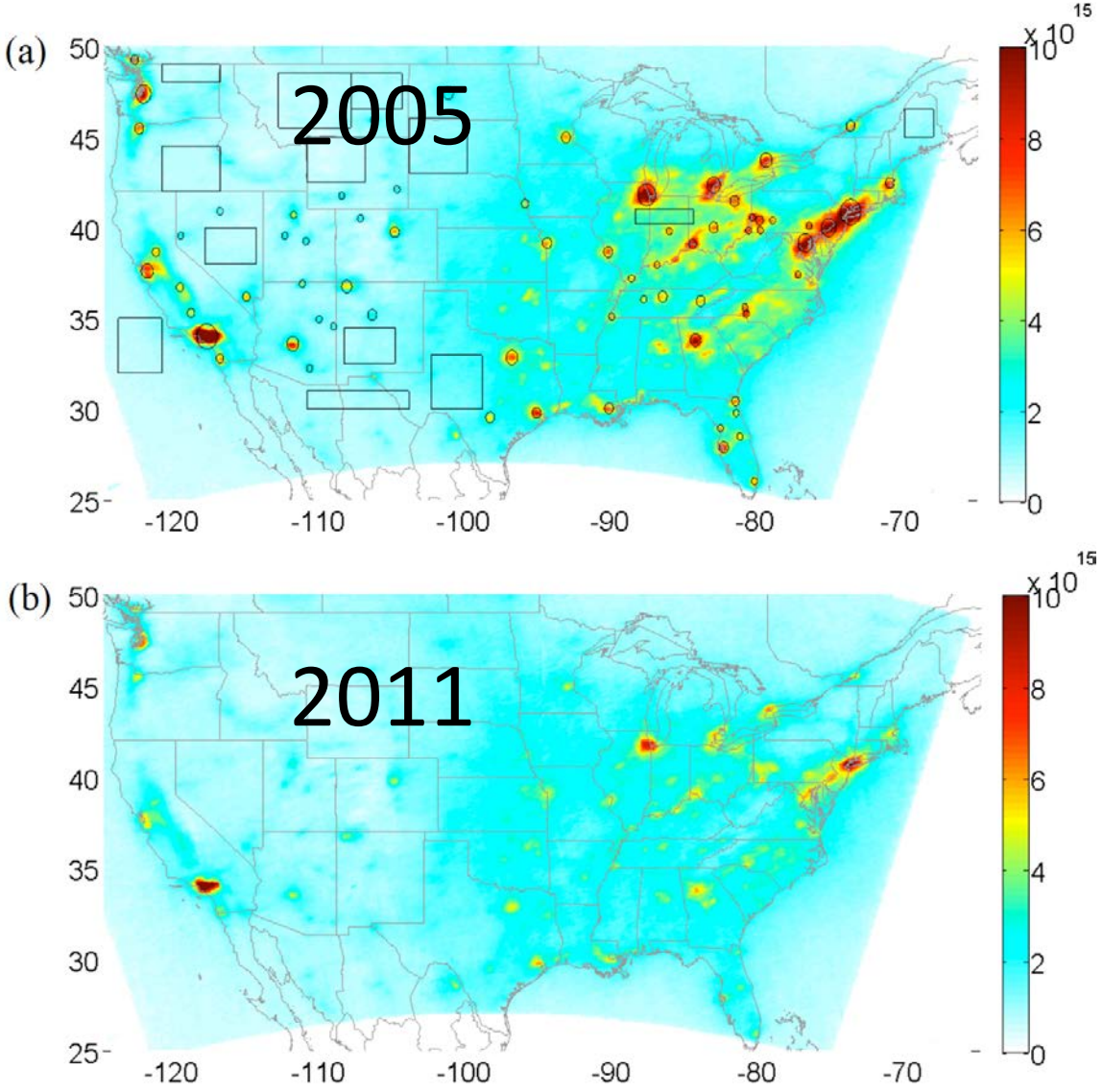

Paulot, et al., Atmos. Chem. Phys., 2012

# The chemical environment of the Southeast US is rapidly changing.

Calculated fate of the isoprene peroxy radical chem (CMAQ)




Rob Pinder, EPA




**Trends in OMI $NO_2$ observations over the United States: effects of emission control technology and the economic recession**

A. R. Russell[1,*], L. C. Valin[1], and R. C. Cohen[1,2]

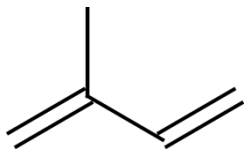
Atmos. Chem. Phys., 12,12197-12209, 2012

# Isoprene

- Large emissions from plants (~500 Tg/yr)
- Can dominate boundary layer OH reactivity
- Potential to form ozone
- Potential to form aerosol

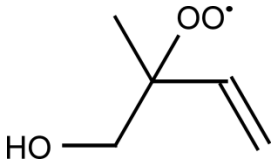
**Pollutant formation is function of $NO_x$ level**

# Isoprene Chemistry



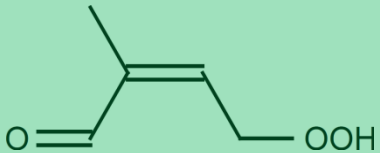
isoprene

+ OH + $O_2$




$RO_2$
(1 of 8)

isom

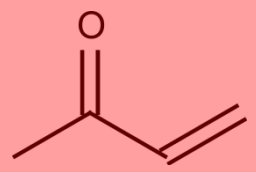



HPALDs
(1 of 2)

yield: unknown

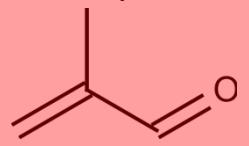
HOx neutral?

NO




MVK

+



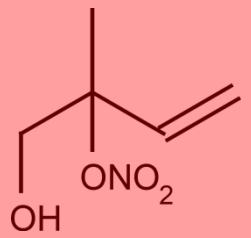

MACR

+

HCHO

~70% yield

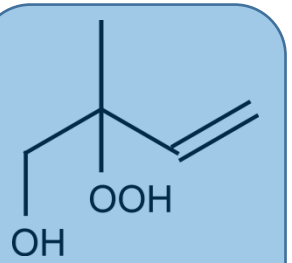
Makes ozone,
Sustains HOx
Aerosol?




ISOPN
(1 of 8)

~10% yield

$HO_2$

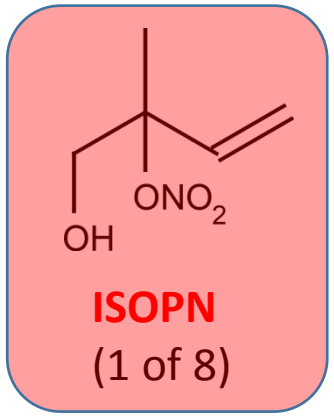



ISOPOOH
(1 of 8)

~90% yield

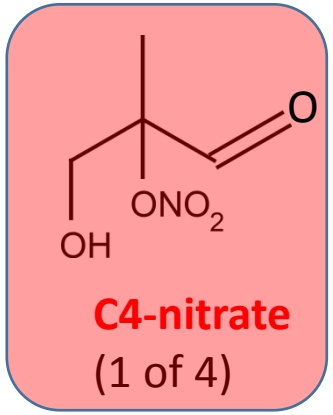
Destroys Ox
Produces known
aerosol precursor

# Further oxidation




**ISOPN**
(1 of 8)

+ OH ↓ k ~ $3x10^{-11}$

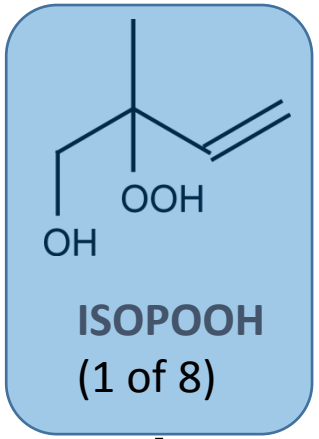



**C4-nitrate**
(1 of 4)

**~70% yield**

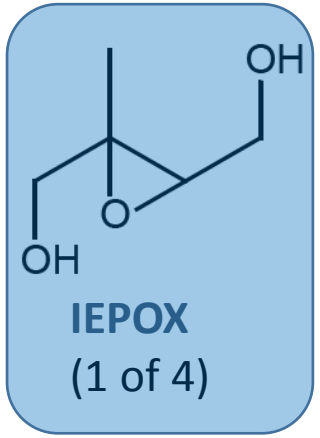
Lee, et al., J. Phys. Chem. A, ASAP, 2014

Tracer for $RO_2$ + NO:
$RO_2$ + NO = (ISOPN+2xC4N)x7




**ISOPOOH**
(1 of 8)

+ OH ↓ k ~ $8x10^{-11}$



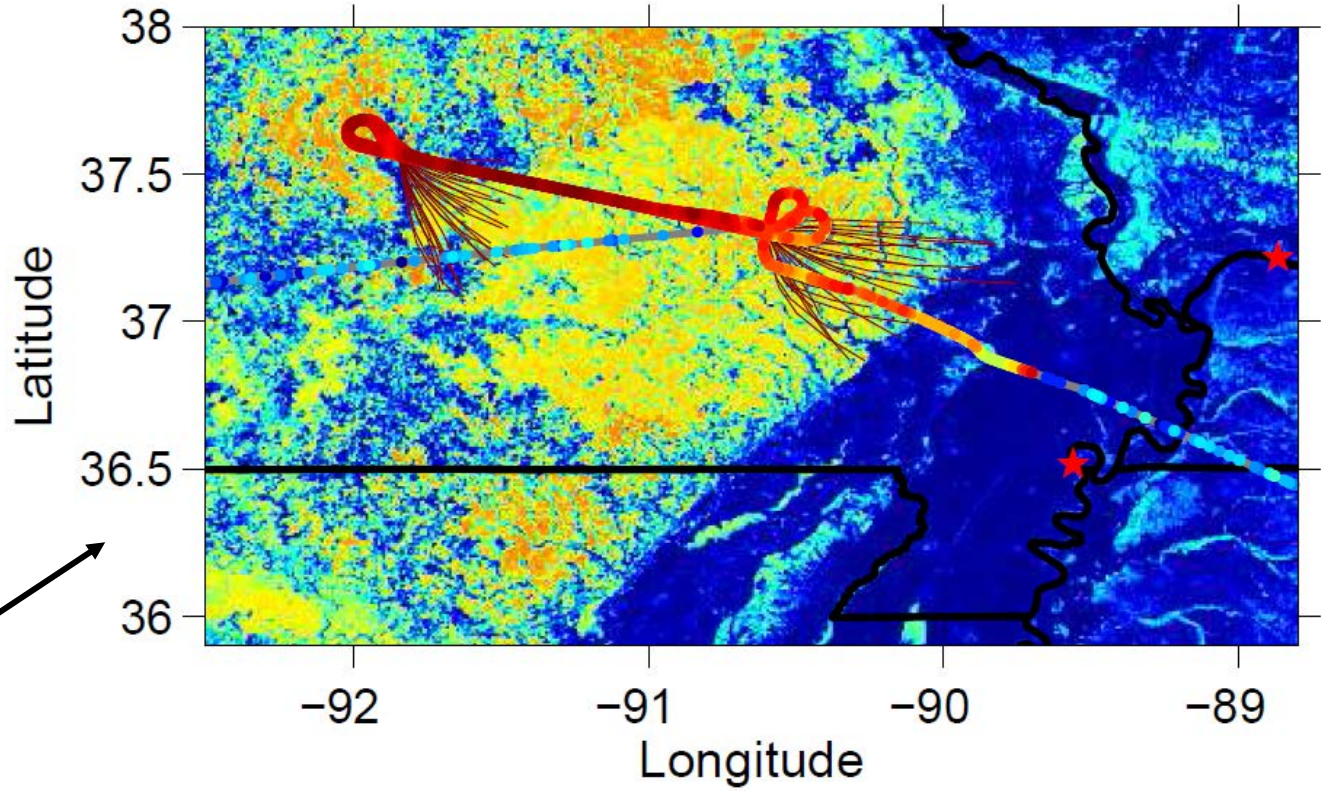

**IEPOX**
(1 of 4)

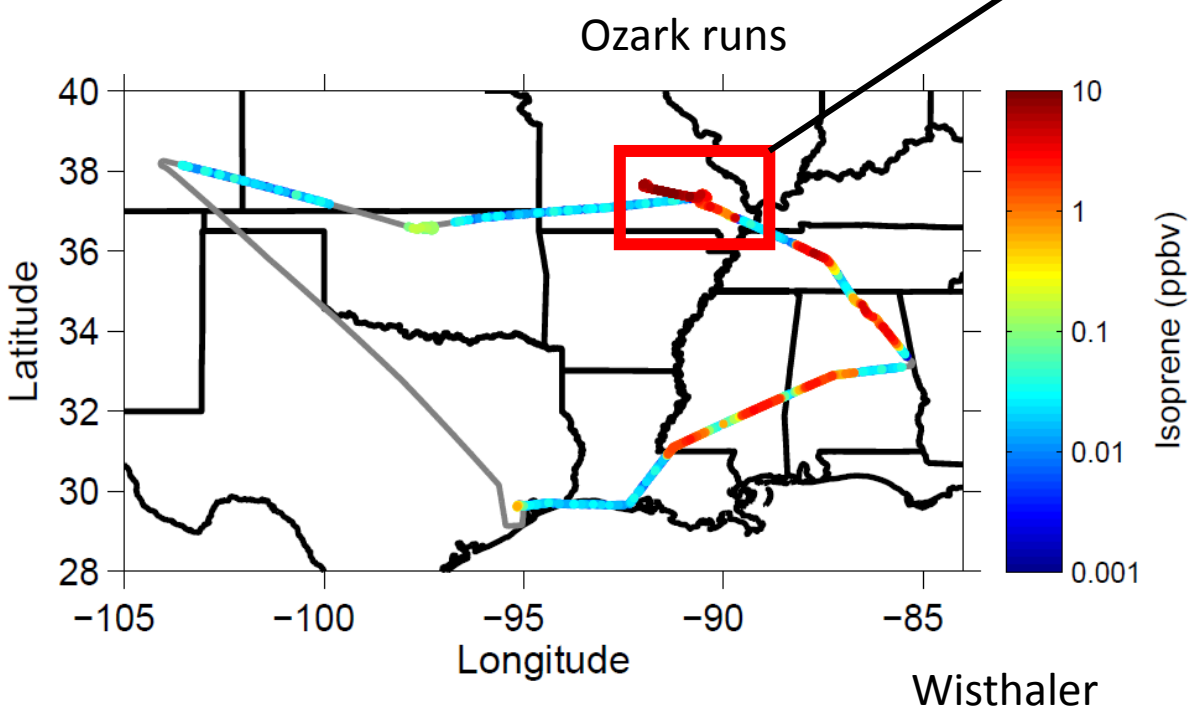
**>70% yield**

St. Clair, et al., in preparation.

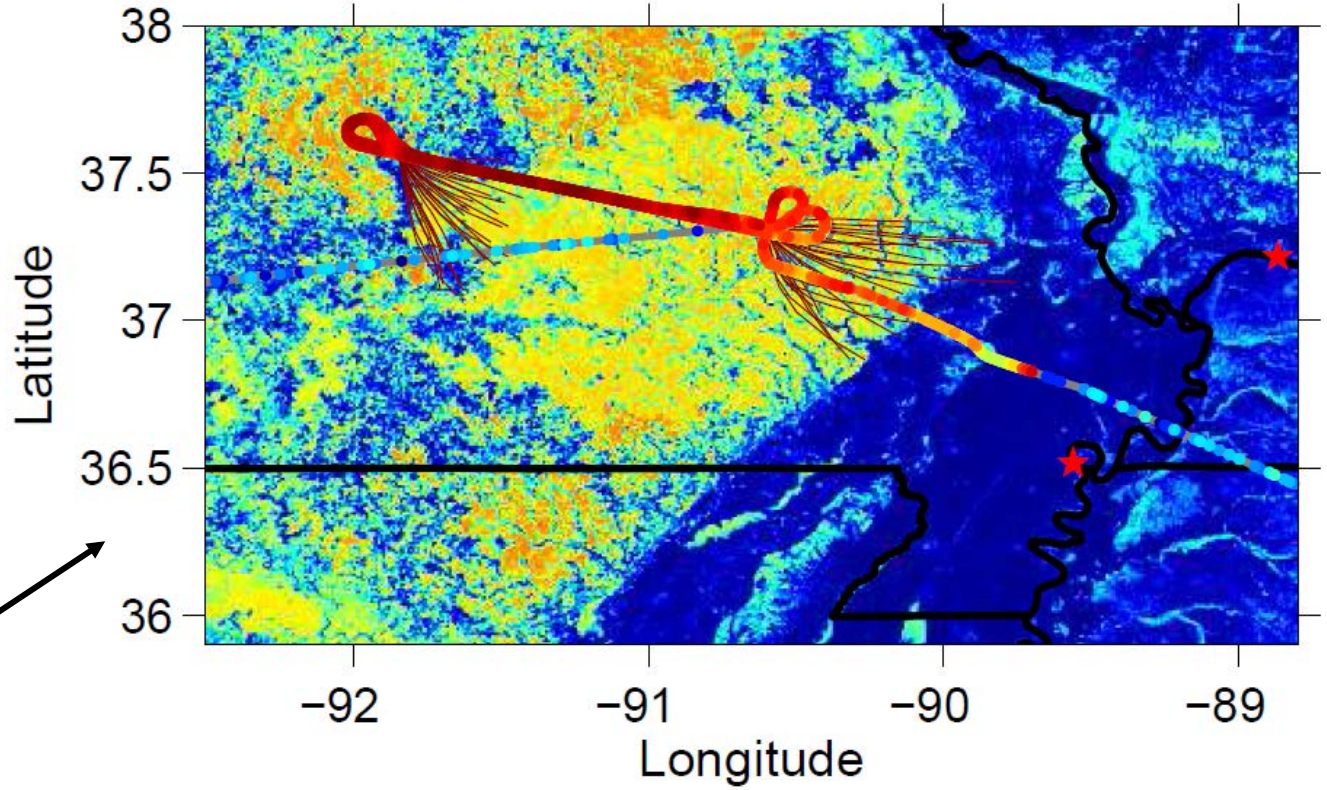
Tracer for $RO_2$ + $HO_2$:
$RO_2$+$HO_2$ = ISOPOOH+IEPOX

# DC8 flight of September 6

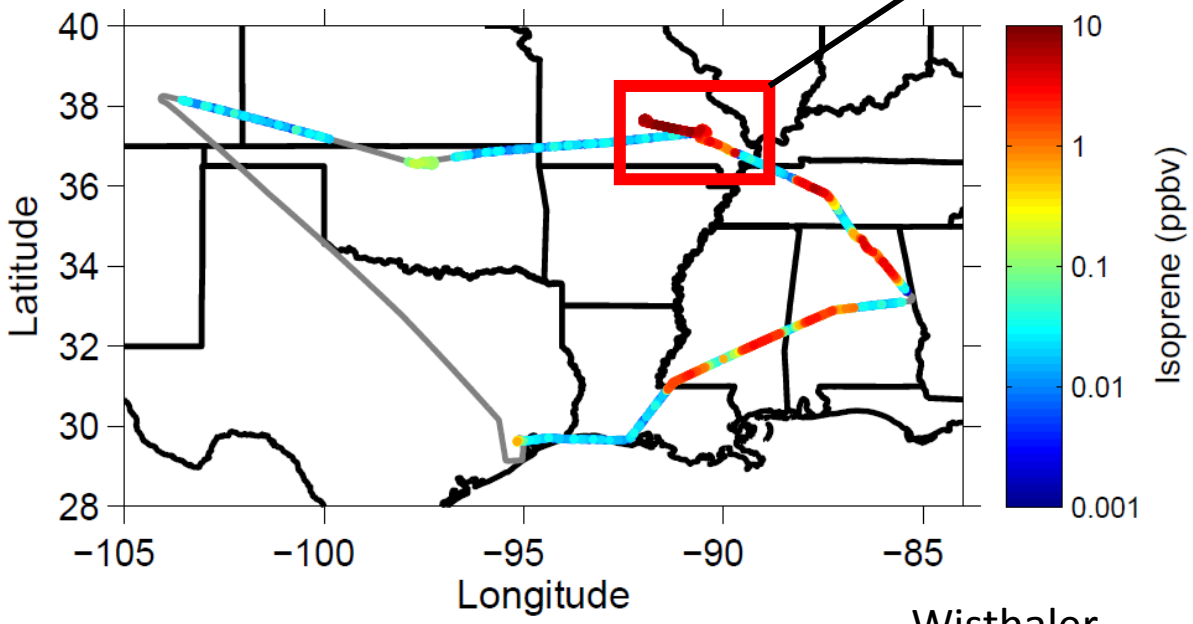


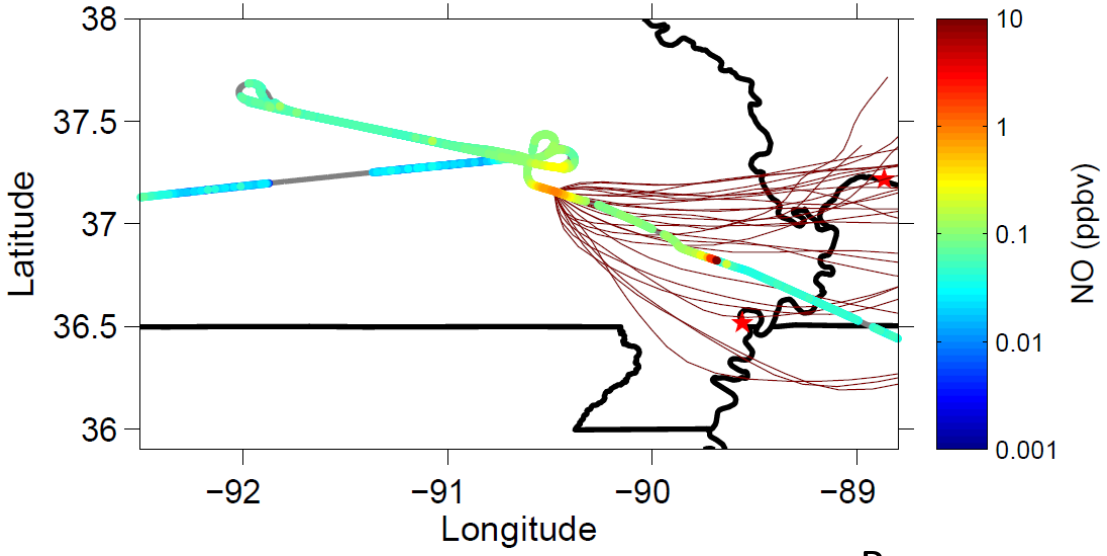
# DC8 flight of September 6




Ozark runs

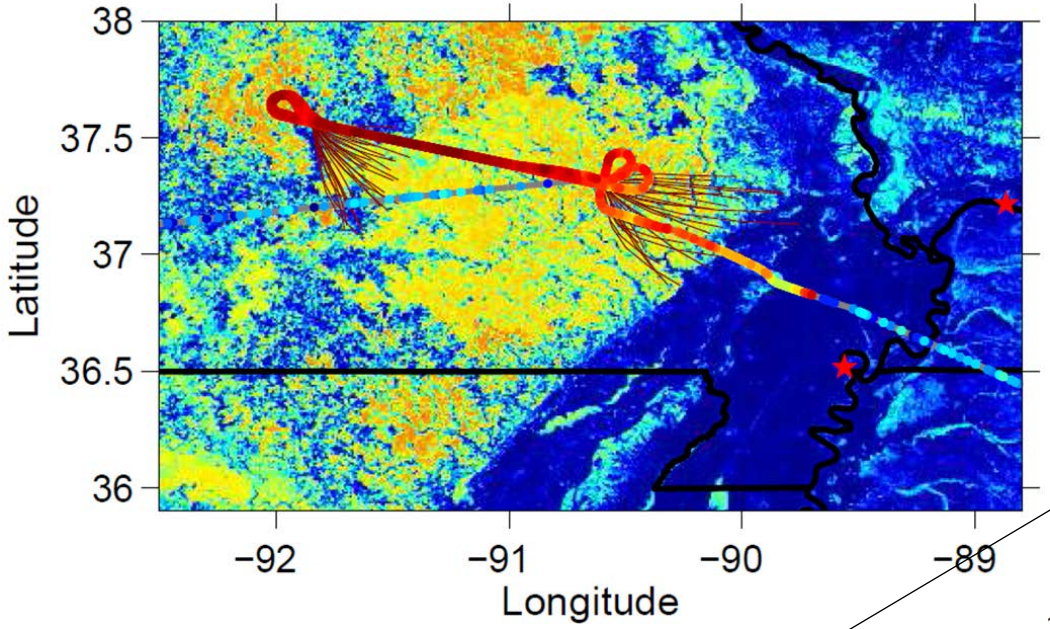


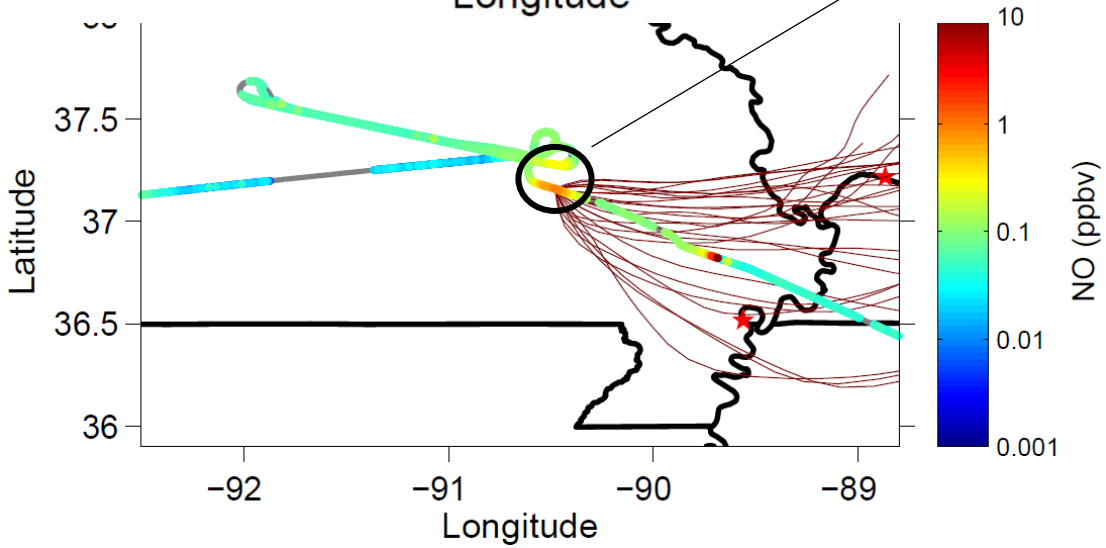

Wisthaler

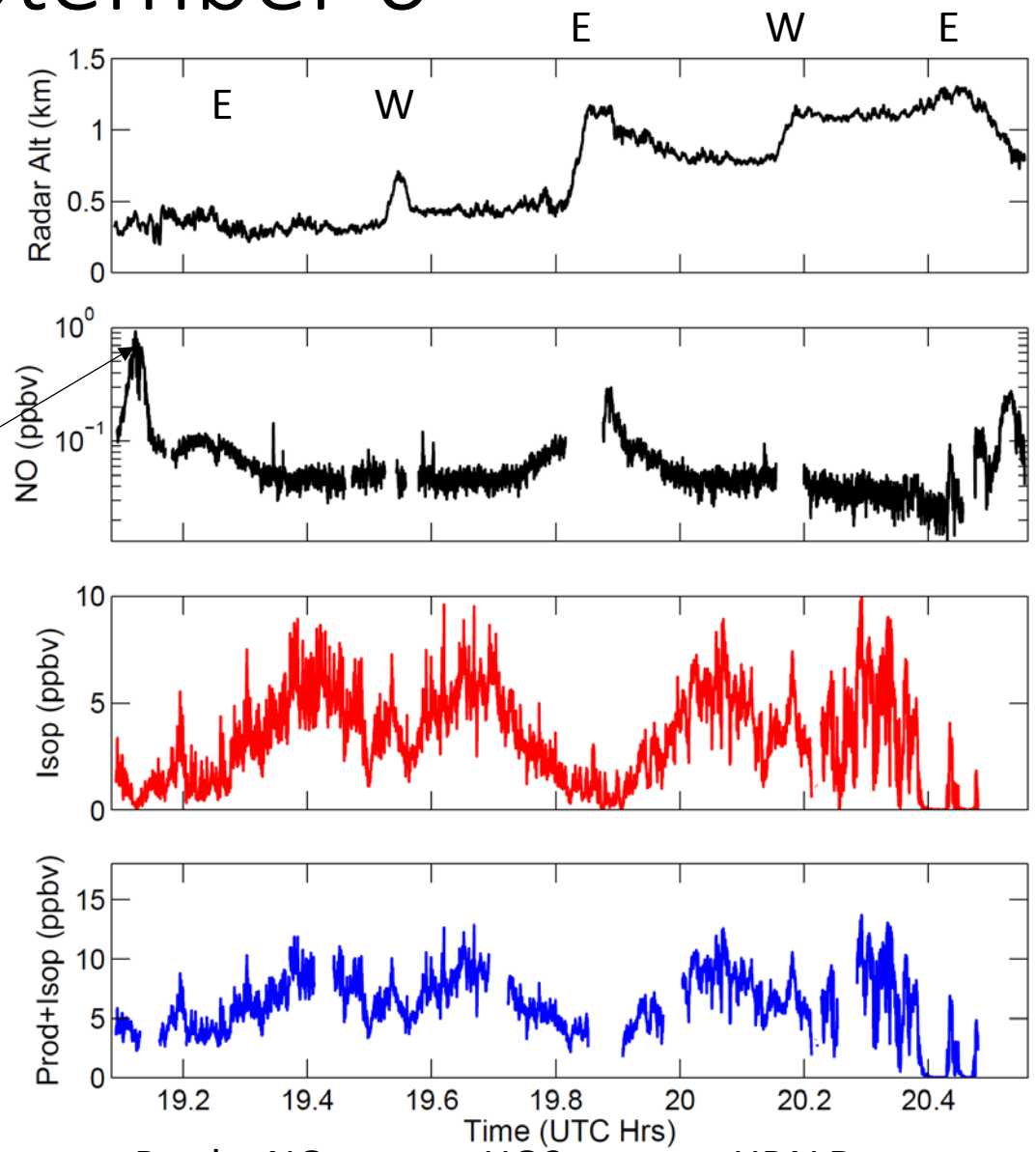



Ryerson

# Timeline Ozark study September 6

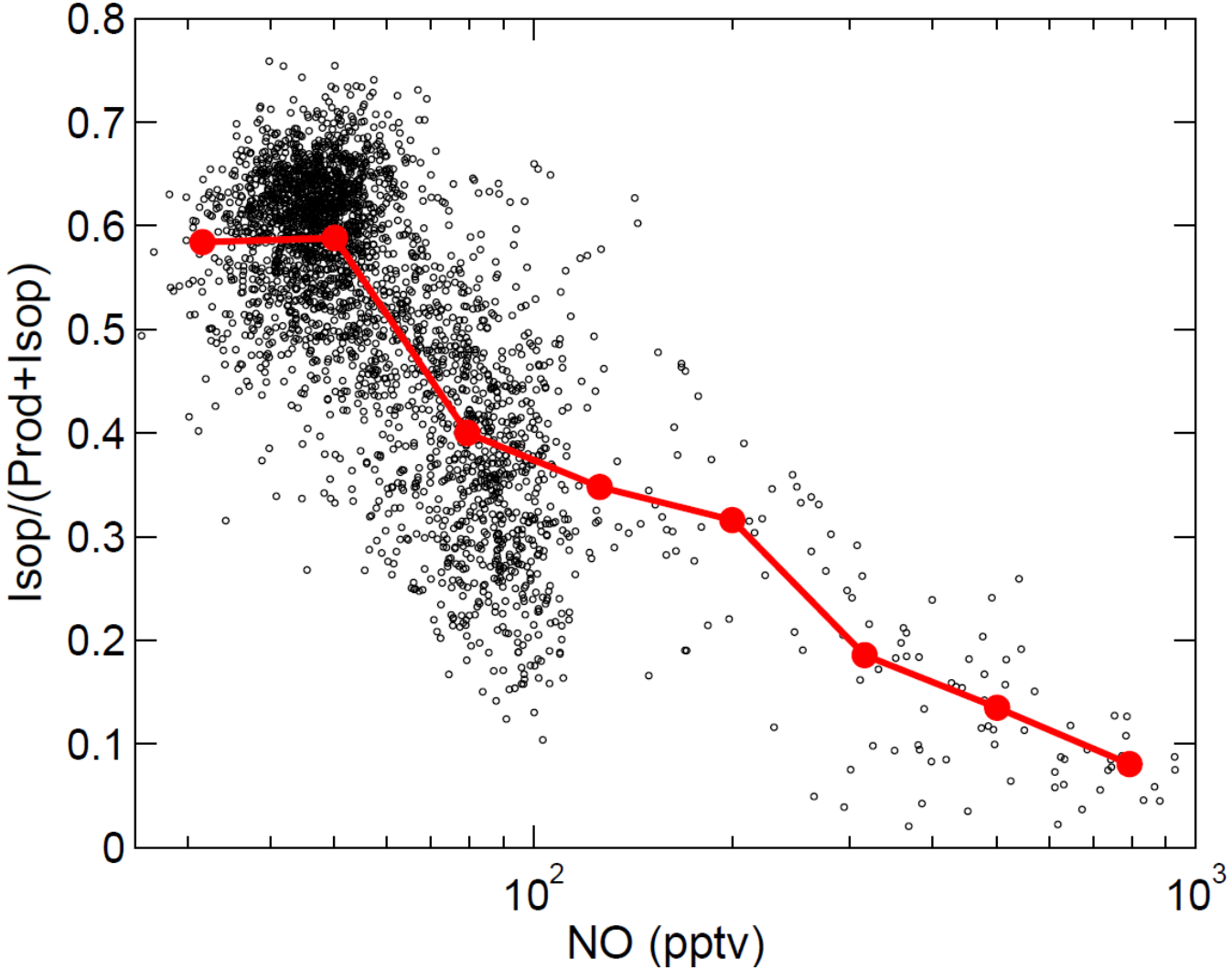


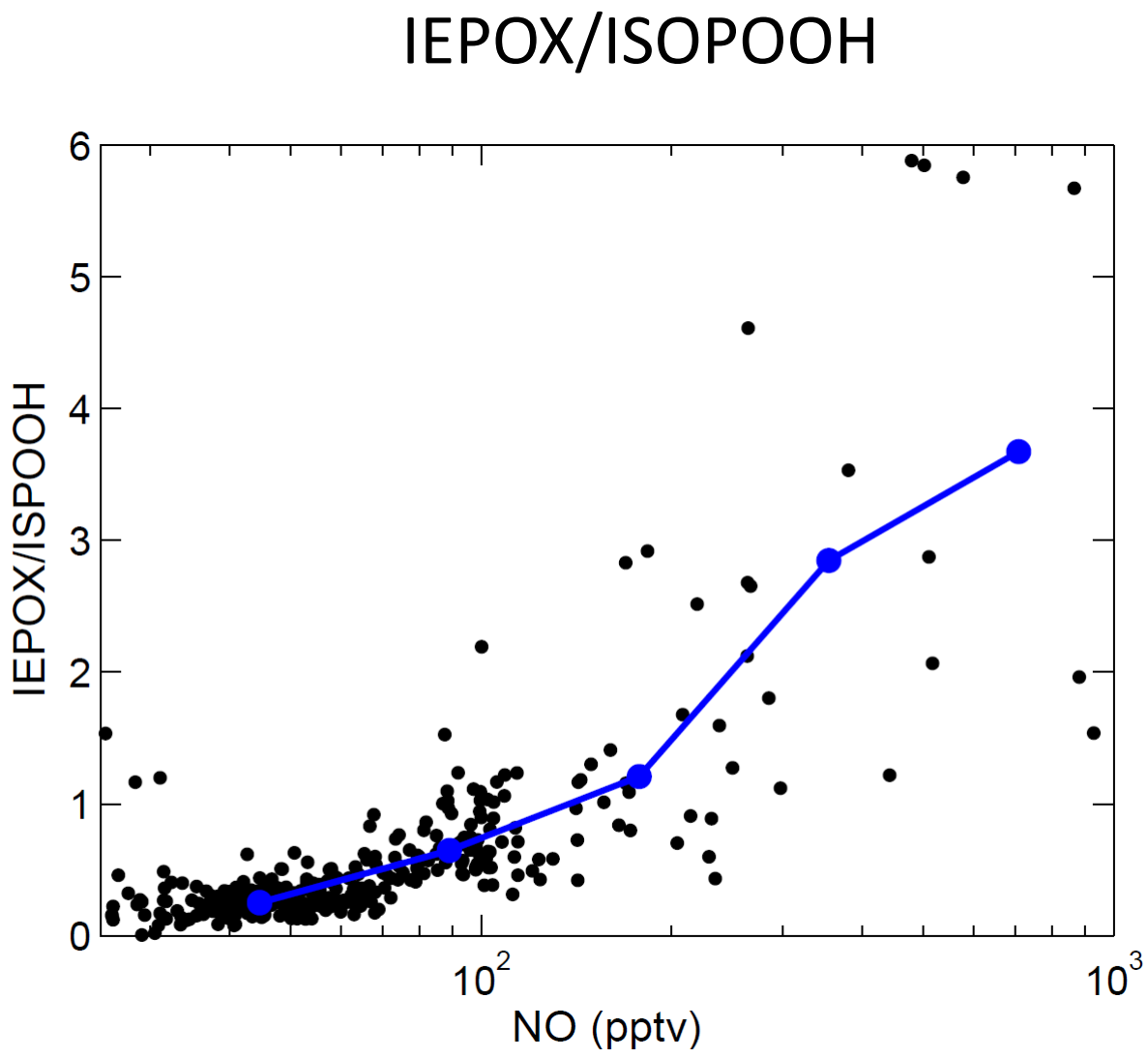



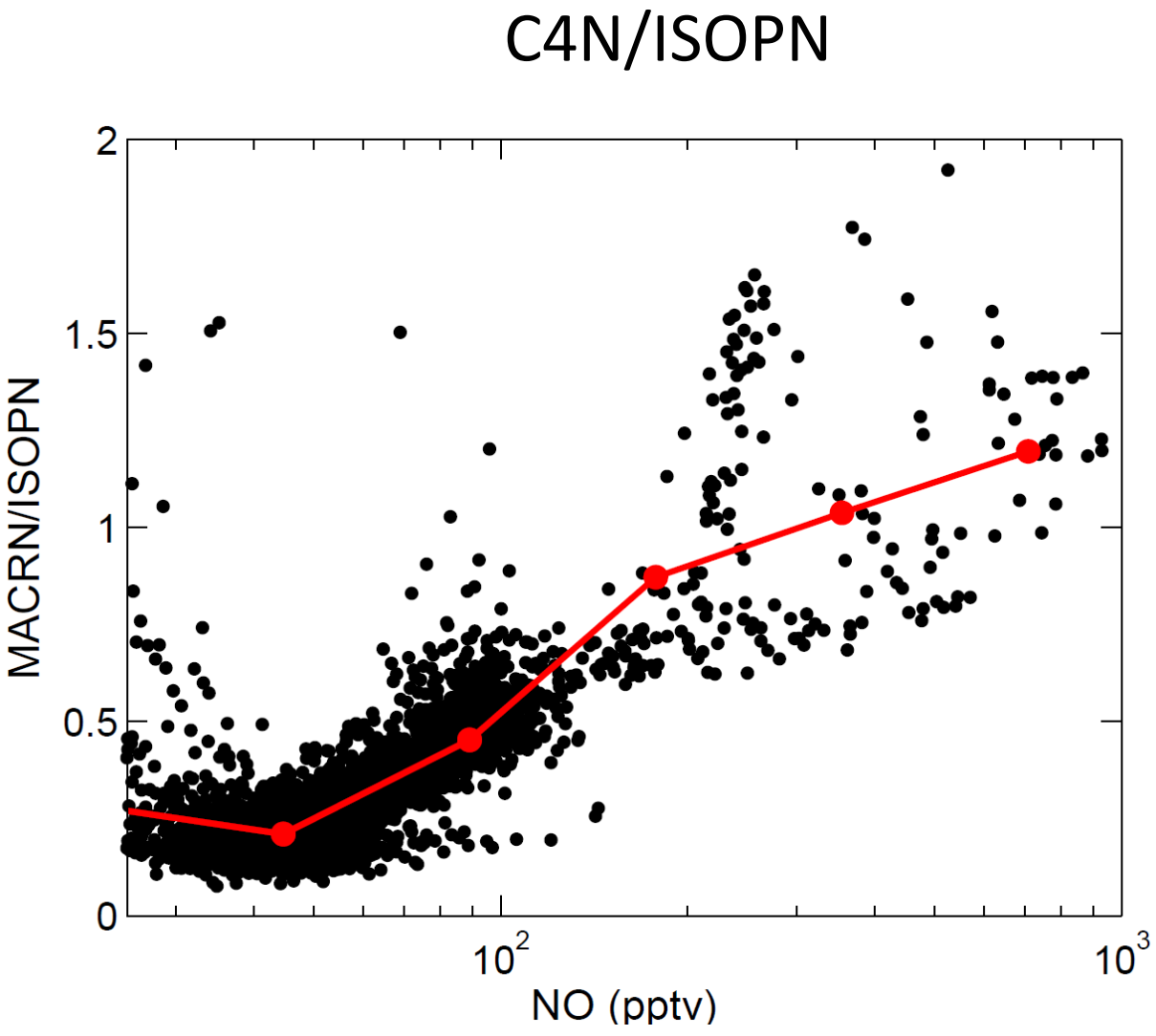




Prod = NO tracer+ HO2 tracer + HPALD

# Isoprene Oxidation Timescale



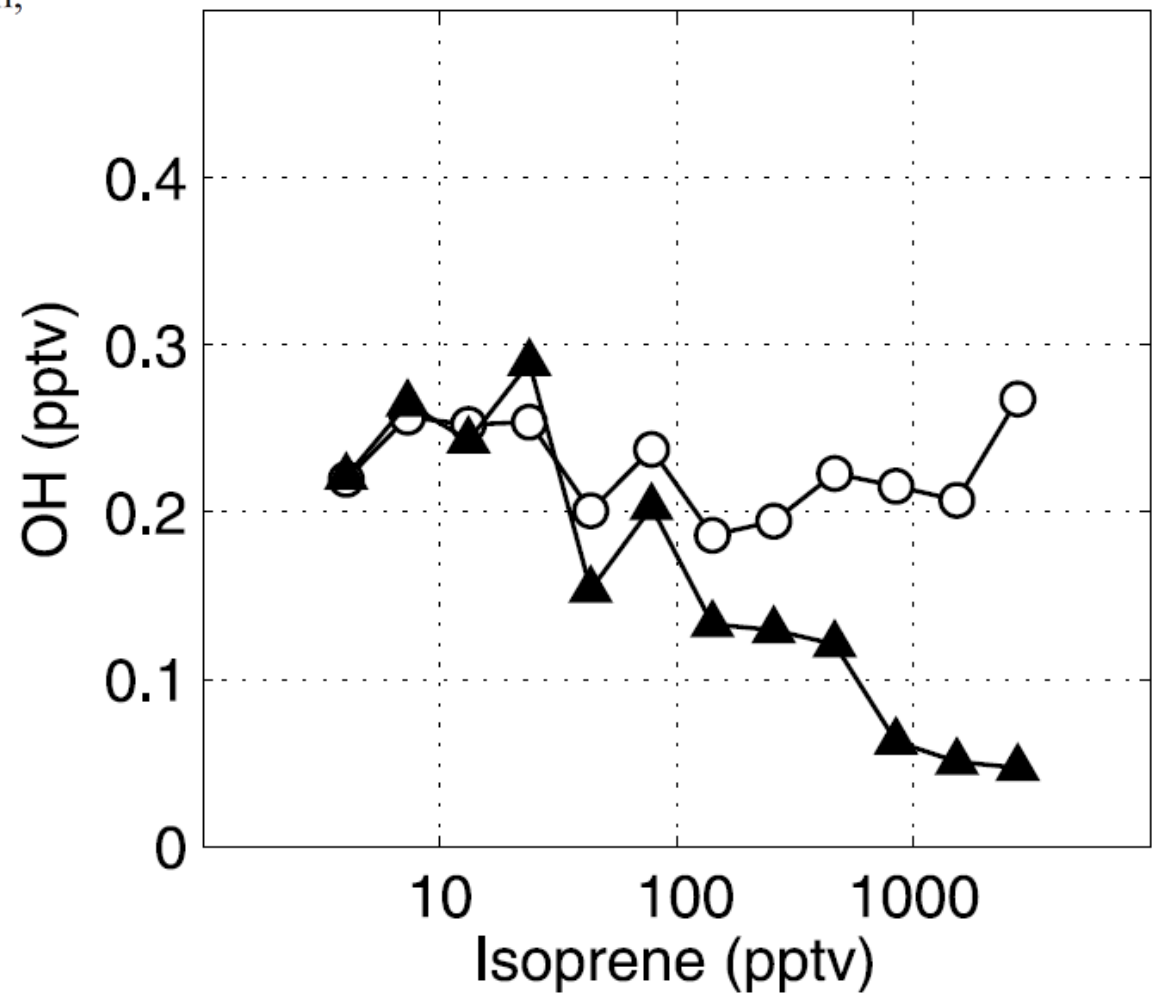

IEPOX/ISOPOOH
IEPOX/ISPOOH
0
1
2
3
4
5
6
$10^2$
$10^3$
NO (pptv)


C4N/ISOPN
MACRN/ISOPN
0
0.5
1
1.5
2
$10^2$
$10^3$
NO (pptv)

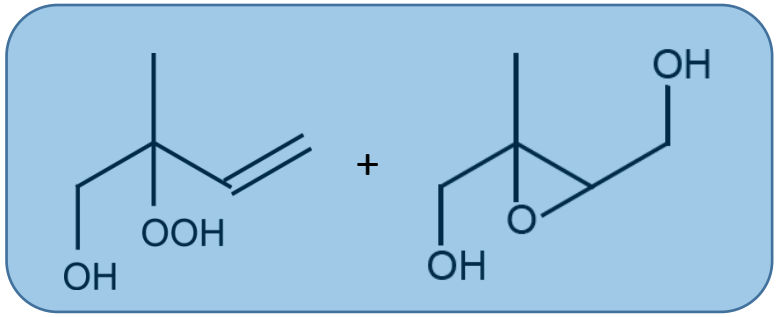
# $HO_x$ chemistry during INTEX-A 2004: Observation, model calculation, and comparison with previous studies

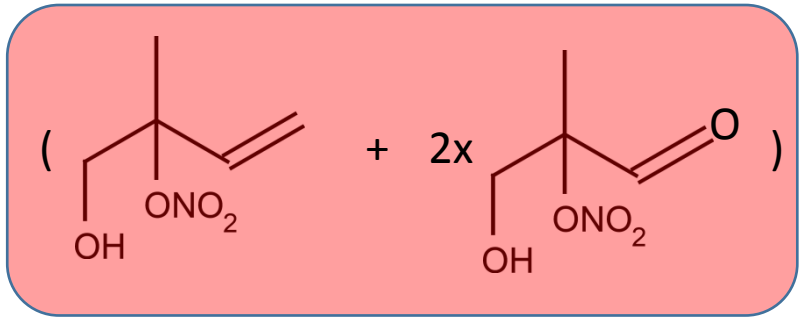
Xinrong Ren,[1,2] Jennifer R. Olson,[3] James H. Crawford,[3] William H. Brune,[1] Jingqiu Mao,[1] Robert B. Long,[1] Zhong Chen,[1] Gao Chen,[3] Melody A. Avery,[3] Glen W. Sachse,[3] John D. Barrick,[3] Glenn S. Diskin,[3] L. Greg Huey,[4] Alan Fried,[5] Ronald C. Cohen,[6] Brian Heikes,[7] Paul O. Wennberg,[8] Hanwant B. Singh,[9] Donald R. Blake,[10] and Richard E. Shetter[11]

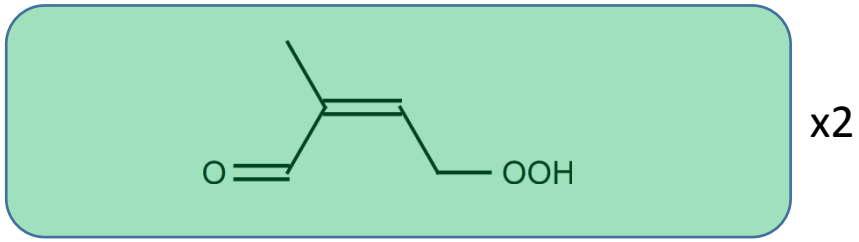
J. Geophys. Res., 113, D05310, 2008.

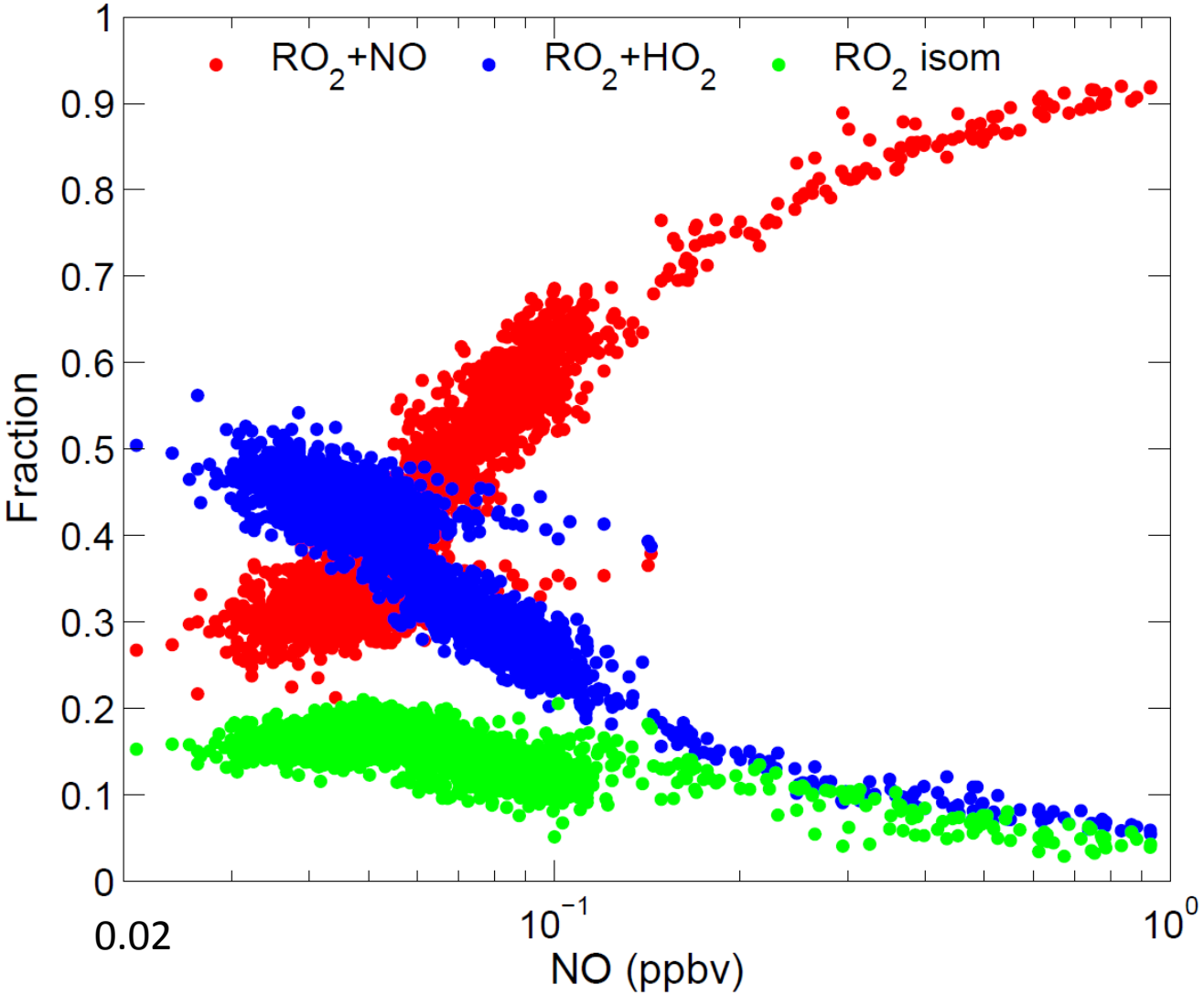


# Isoprene $RO_2$ reaction partners (from products)

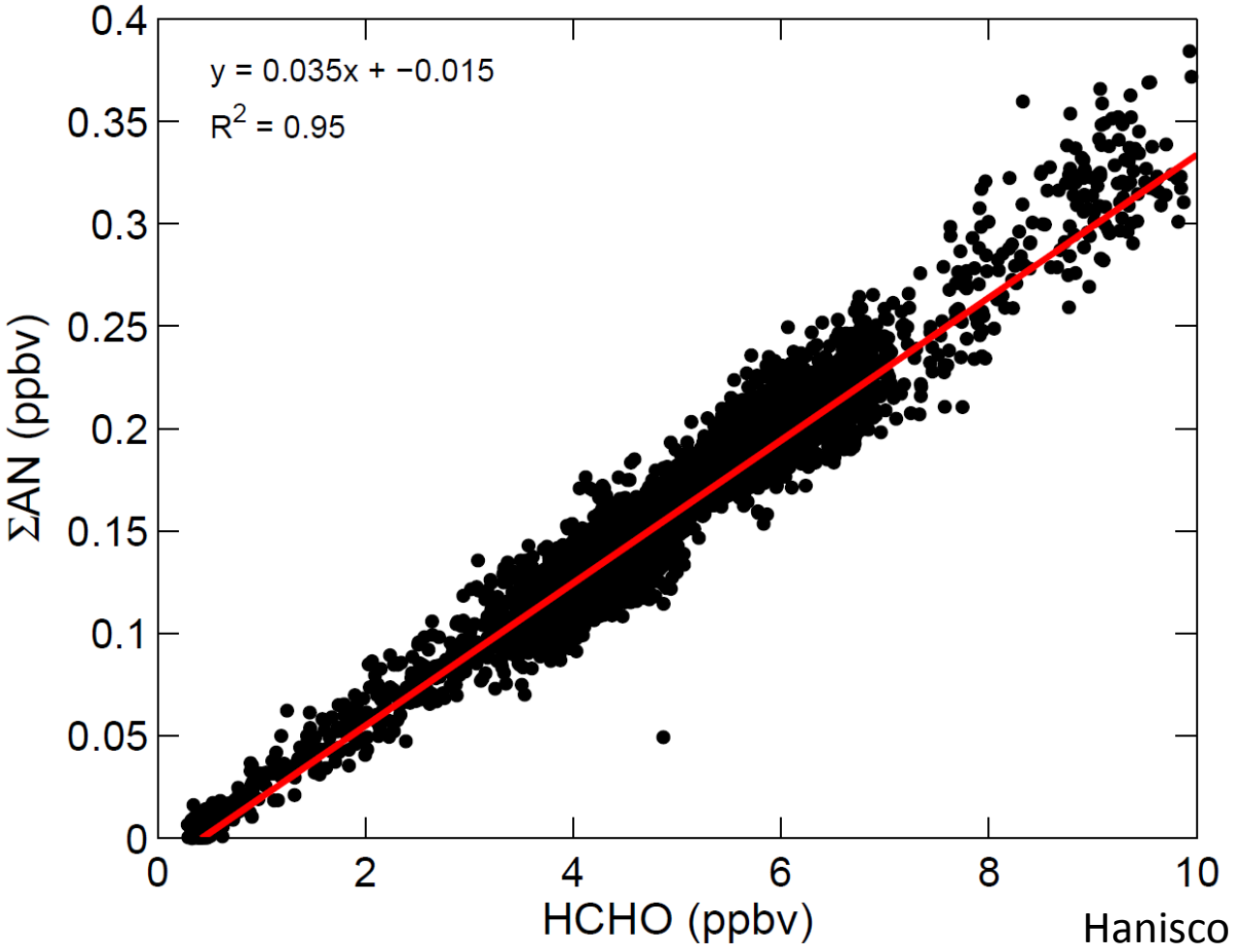


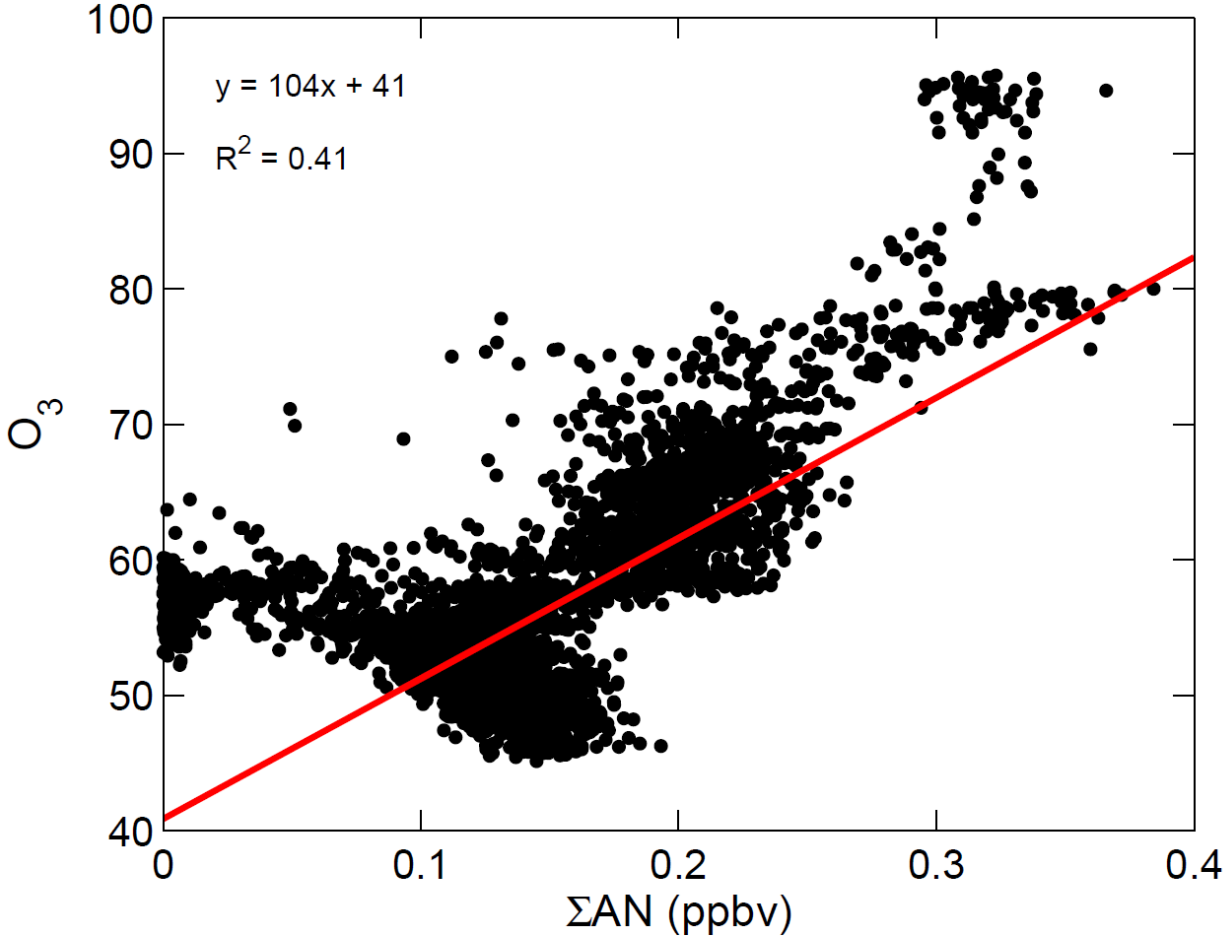
# Isoprene derived nitrates vs. HCHO




Hanisco

ΣAN = ISOPN + C4N + PROPNN + ETHLN

# Isoprene derived nitrates vs. ozone




Mao, J, et al., J. Geophys. Res.-Atmos., 118, 1-13, 2013

# Conclusions

- Oxidants are significantly impacted by isoprene chemistry .
- The impacts are regulated by the ratio of the flux of NOx to isoprene emitted into the atmosphere
- NOx emissions are declining across the US. This decline drives more of the isoprene chemistry through low-NO pathways leading to less ozone and unknown but likely important changes in aerosol.
- SEAC4RS provides a suite of observations to evaluate our description of isoprene chemistry --observations from Caltech provide key measures of the branching between these pathways.

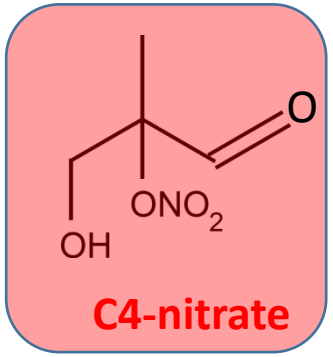
# Acknowledgements


- Tom Ryerson – NOx and $O_3$
- Armin Wisthaler – Isoprene
- Tom Hanisco – Formaldehyde
- Rob Pinder and Havela Pye – CMAQ modeling
- Fight Planners and flight crew – For thoughtful planning and remarkable execution of meaningful experiments
- SEAC4Rs science team – For a very rich data set
- NASA – Funding

# Fast photolysis of carbonyl nitrates from isoprene

J.-F. Müller[1], J. Peeters[2], and T. Stavrakou[1]

Atmos. Phys. Chem., 14, 2497-2508, 2014




$J = 3.5e\text{-}4\ s^{-1}$ →

HAC + HCHO + $HO_2$

$\tau_{photo} = 45$ min