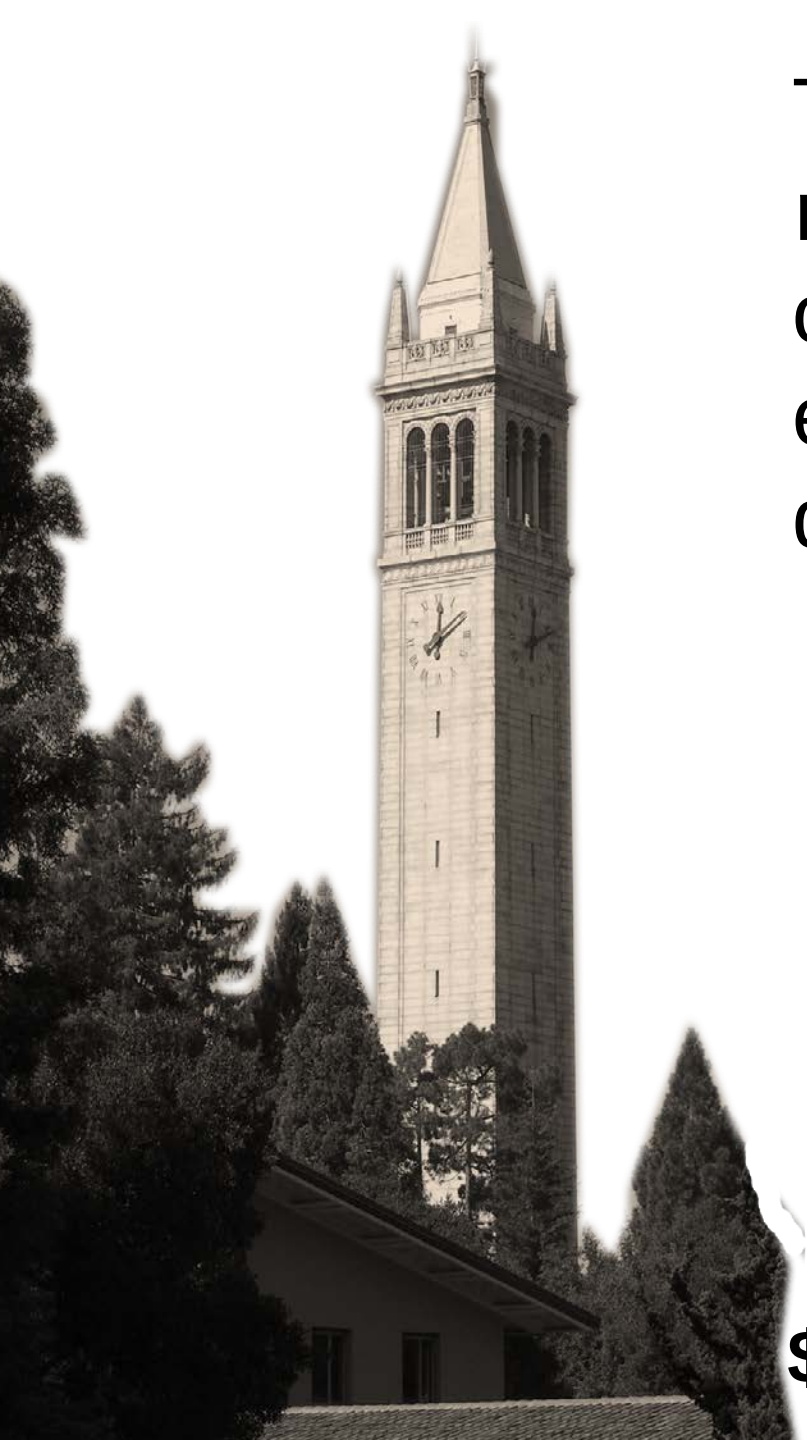
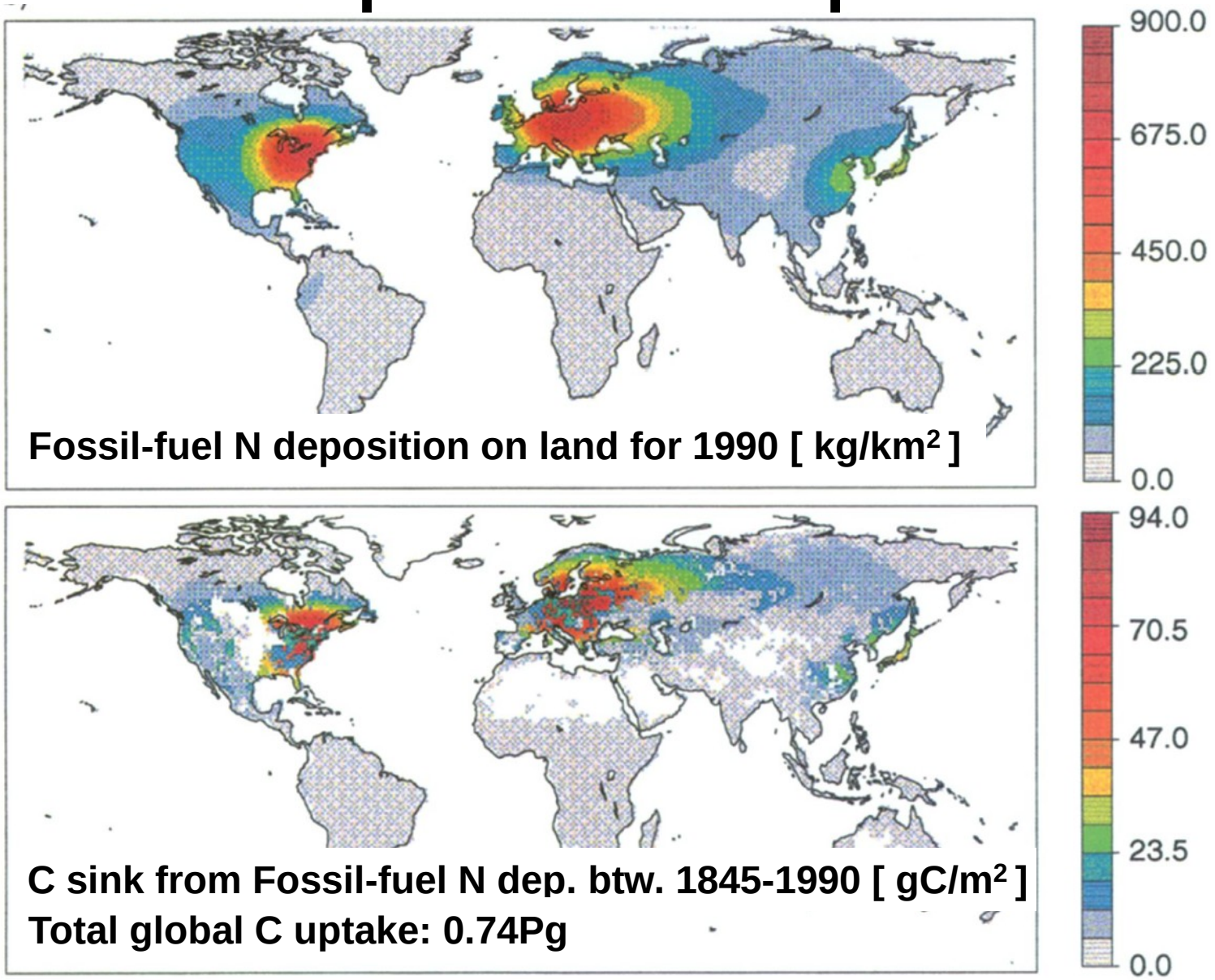


Thoughts on mechanisms of oxidized nitrogen emission and deposition

Ronald C. Cohen
October 2013

$$ NSF-AGS; NASA

N deposition & C uptake [Townsend et al., 1996]



Fossil-fuel N deposition on land for 1990 [kg/km^2]

C sink from Fossil-fuel N dep. btw. 1845-1990 [gC/m^2]

Total global C uptake: 0.74Pg

We think we know the global budget reasonably well

Global NO_x Sources

$NO_x \equiv NO + NO_2$

Source	*Tg N year $^{-1}$*
Fuel Consumption	26
Biomass Burning	6
Soil Emission	9
Lightning	5
Total	46

Jaegle et al. *Faraday Discussions*,, **2005**
Schumann and Huntreiser, ACPD **2007**

Direct observational evidence for specific processes is more ambiguous

Emissions

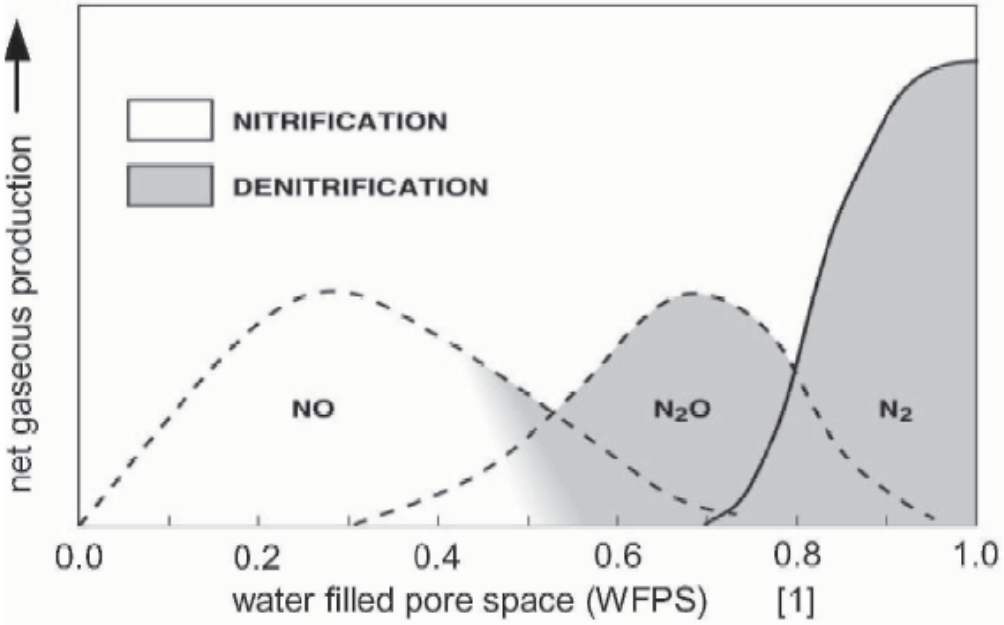
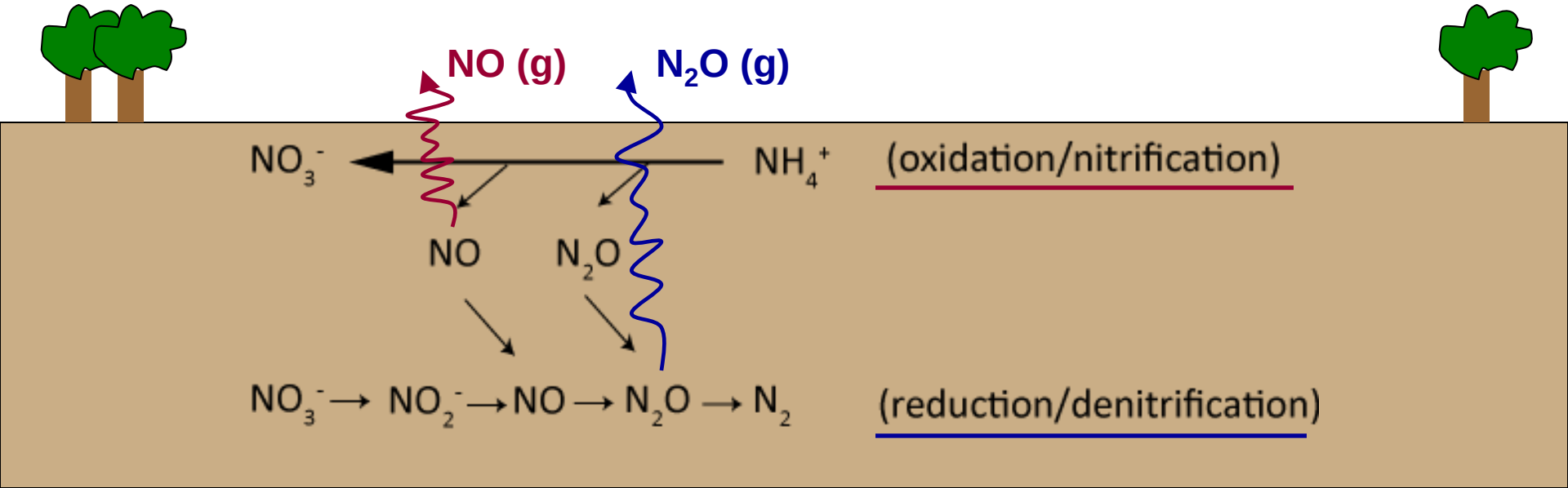
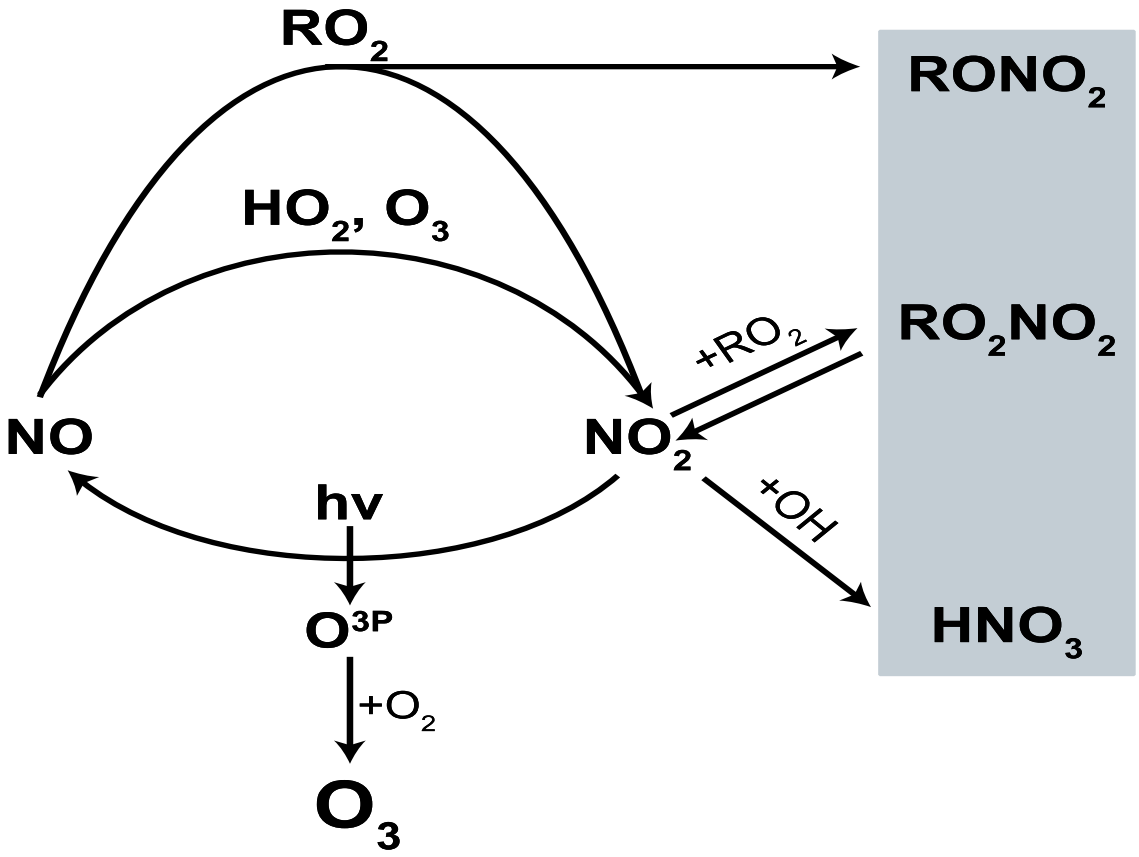


Figure from
Meixner and Yang, Dryland Ecohydrology, 2006



Atmospheric Chemistry



Questions/issues

1. Global models find mechanistic models of soil emissions are too large.

To deal with this problem they introduce an ad hoc canopy reduction factor that removes as much as 80% of emissions that start at soils before they get to the free troposphere.

This CRF only acts on emitted NOx, not any other NOx that might enter the canopy.

Questions/issues

2. Laboratory measurements suggest ecosystems emit NO_x directly when ambient concentrations are low.

Note most measurements by ecologists in Teflon chambers seemingly unaware of atmospheric chemistry literature showing chamber materials themselves are a source of NO_x.

"NOx Flux Conundrum" Lerdau, Munger and Jacob, Science 2000

Questions/issues

3. Most field instruments for observing nitrogen oxides have positive artifacts

All but a few of the long term records of "NO_2" in the world are by instruments that measure the sum of NO_2, PAN-like molecules, $RONO_2$ and an indeterminate fraction of HNO_3.

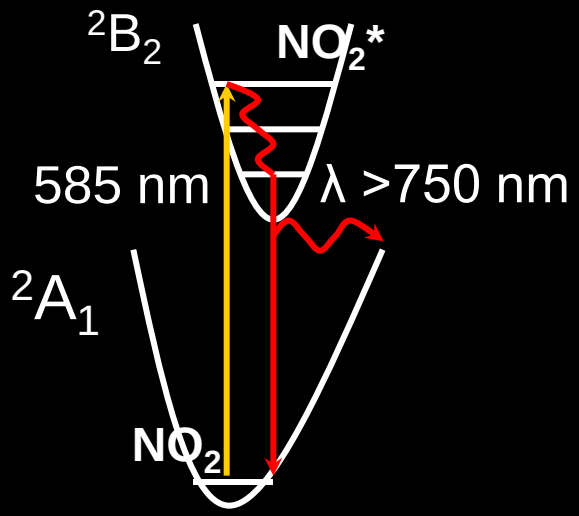
Many of the "HNO_3" measurements are sums of HNO_3, and $RONO_2$. Or at least of the fraction of $RONO_2$ where R includes an –OH group (e.g. isoprene derived nitrates).

Questions/issues

4. Until the last couple of years (and now only in the state-of-the-art research models), isoprene and monoterpene chemistry was so poorly represented that model-measurement comparisons that depend on having gas or aerosol chemistry right are not interpretable as mechanistic descriptions of the fate of NO_x.

Note NO_x emissions are often tuned to get the O_3 right and not the NO_x.

LIF Detection of NO_2



White cell configuration with ~30 passes.
Detection cell pressures 50-250 mTorr.

Vacuum pump

7kHz Pulsed
Nd:YAG

NO_2 reference cell

PMT

PMT

532 nm

Tunable Dye Laser

585 nm

Multipass Cell #1

Multipass Cell #2

Nozzles for supersonic expansion

Gas in - 200-760torr (ambient pressure)

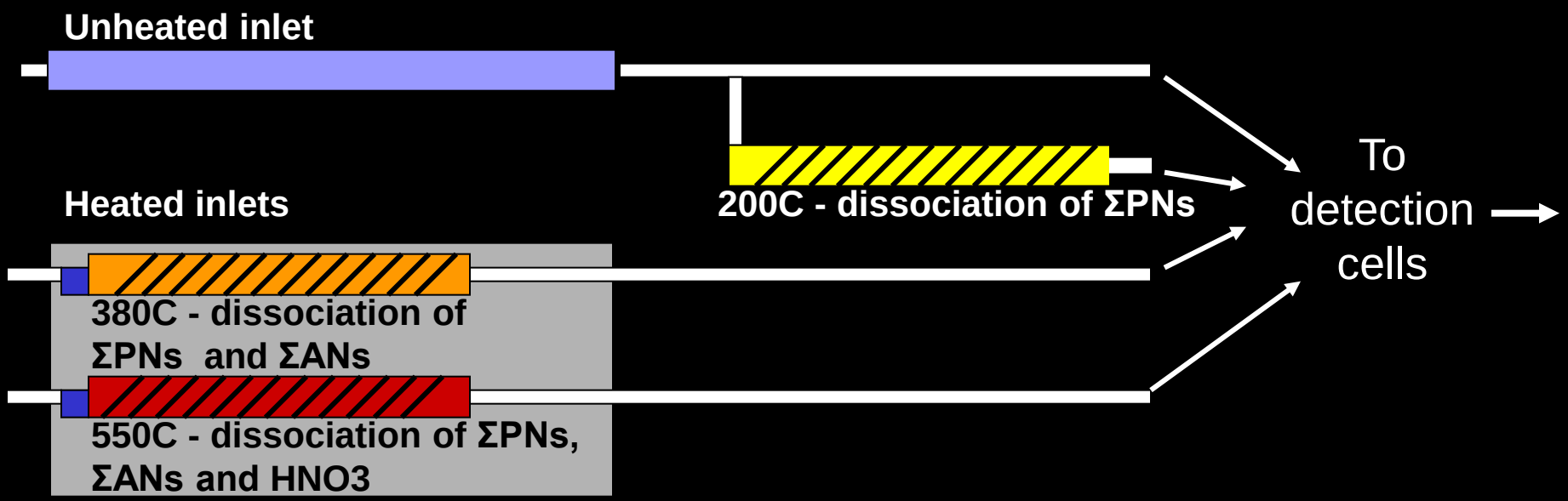
Thermal Dissociation

followed by LIF detection of resulting NO_2 to infer ΣPNs, ΣANs and HNO_3

XNO_2 + heat → NO_2 + X

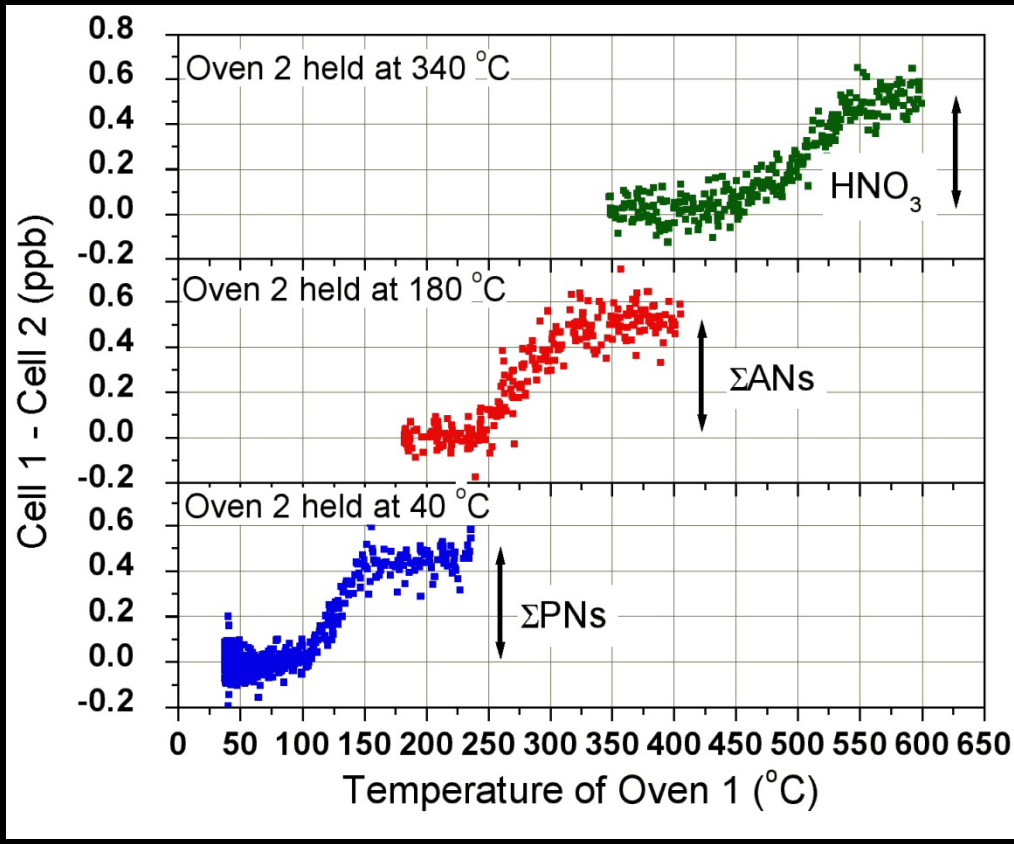
X = OH, RO or RO_2

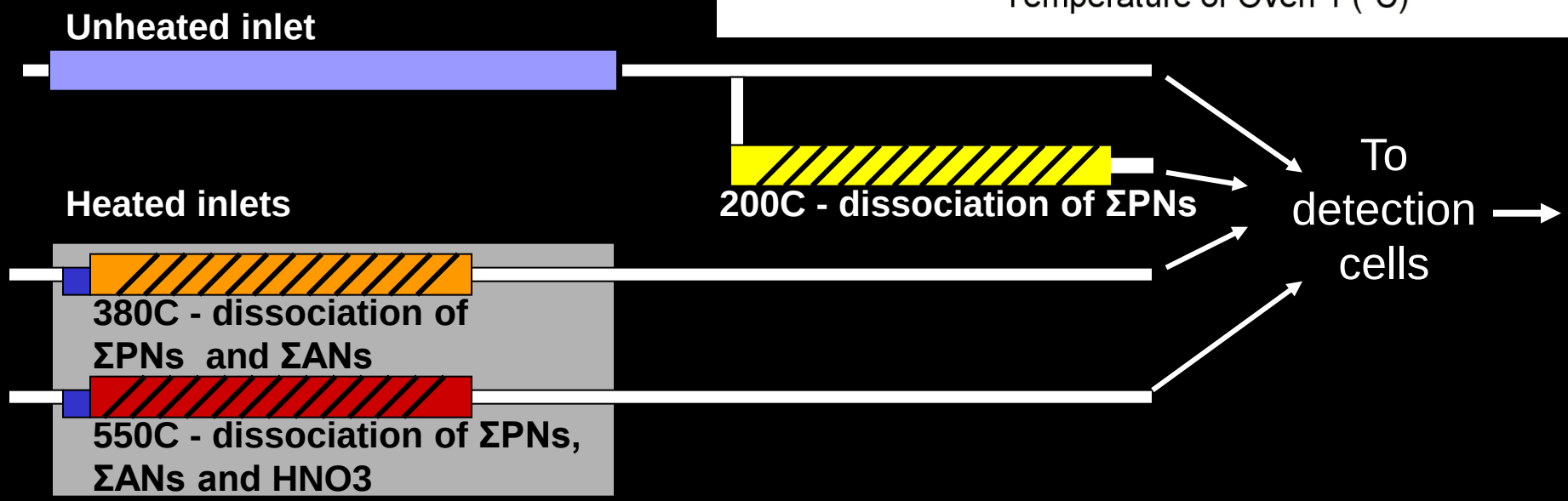
Differing bond strengths lead to dissociation at characteristic temperatures



Thermal Dissociation

followed by LIF detection of resulting NO_2 to infer ΣPNs, ΣANs and HNO_3





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

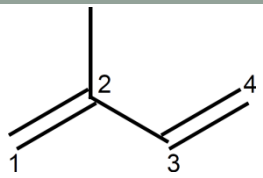
$$RO_2 + NO \xrightarrow{M} RONO_2 \qquad \alpha$$

Urban locations: Alkanes (C_6 and larger), Alkenes, Aromatics, biogenics

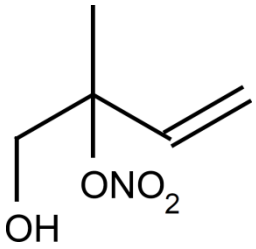
Rural locations: Isoprene and monoterpenes

Oil and Gas regions: Alkanes

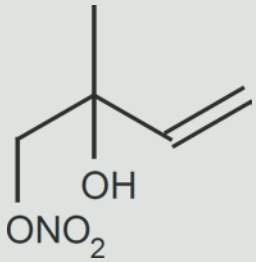
The nitrates



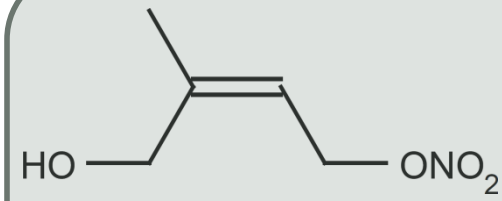
isoprene



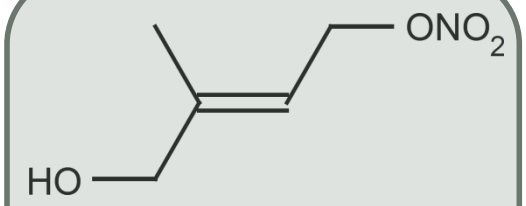
1-OH-2-ONO$_2$



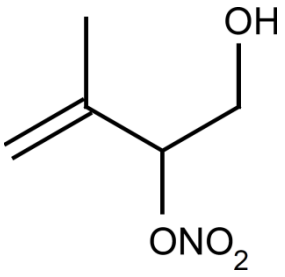
2-OH-1-ONO$_2$



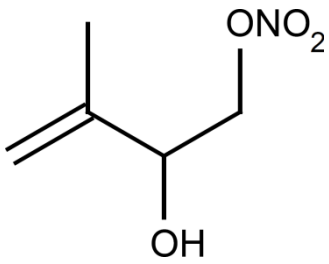
Z-1-OH-4-ONO$_2$



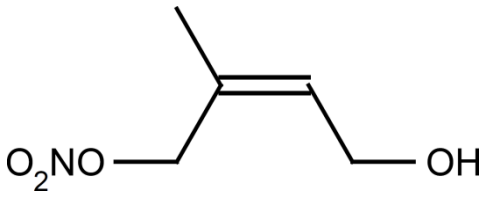
E-1-OH-4-ONO$_2$



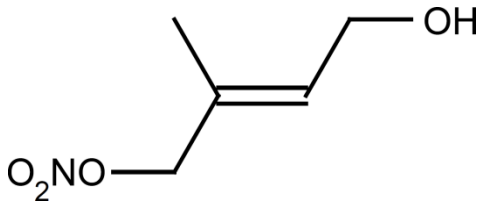
4-OH-3-ONO$_2$



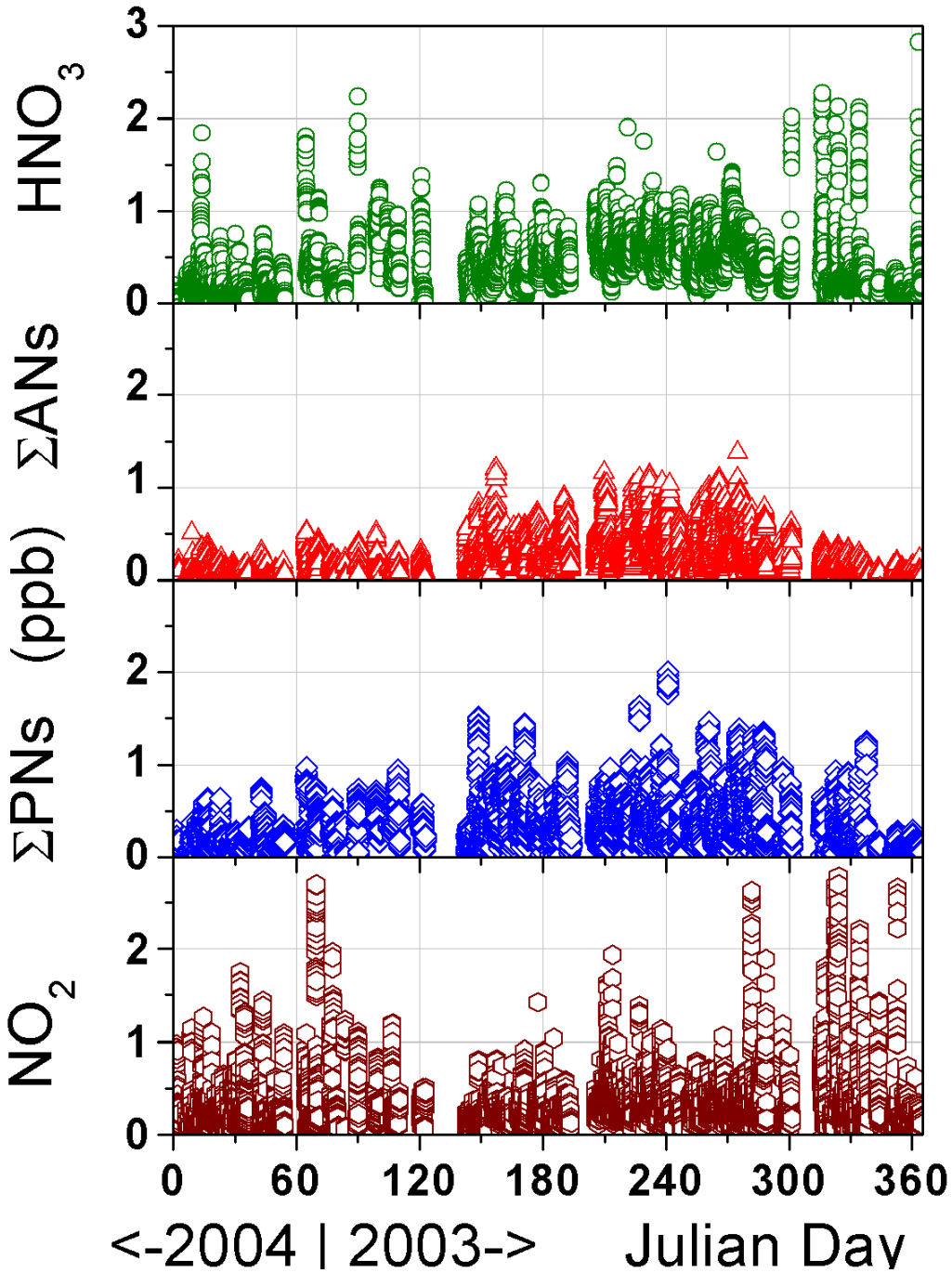
3-OH-4-ONO$_2$



Z-4-OH-1-ONO$_2$



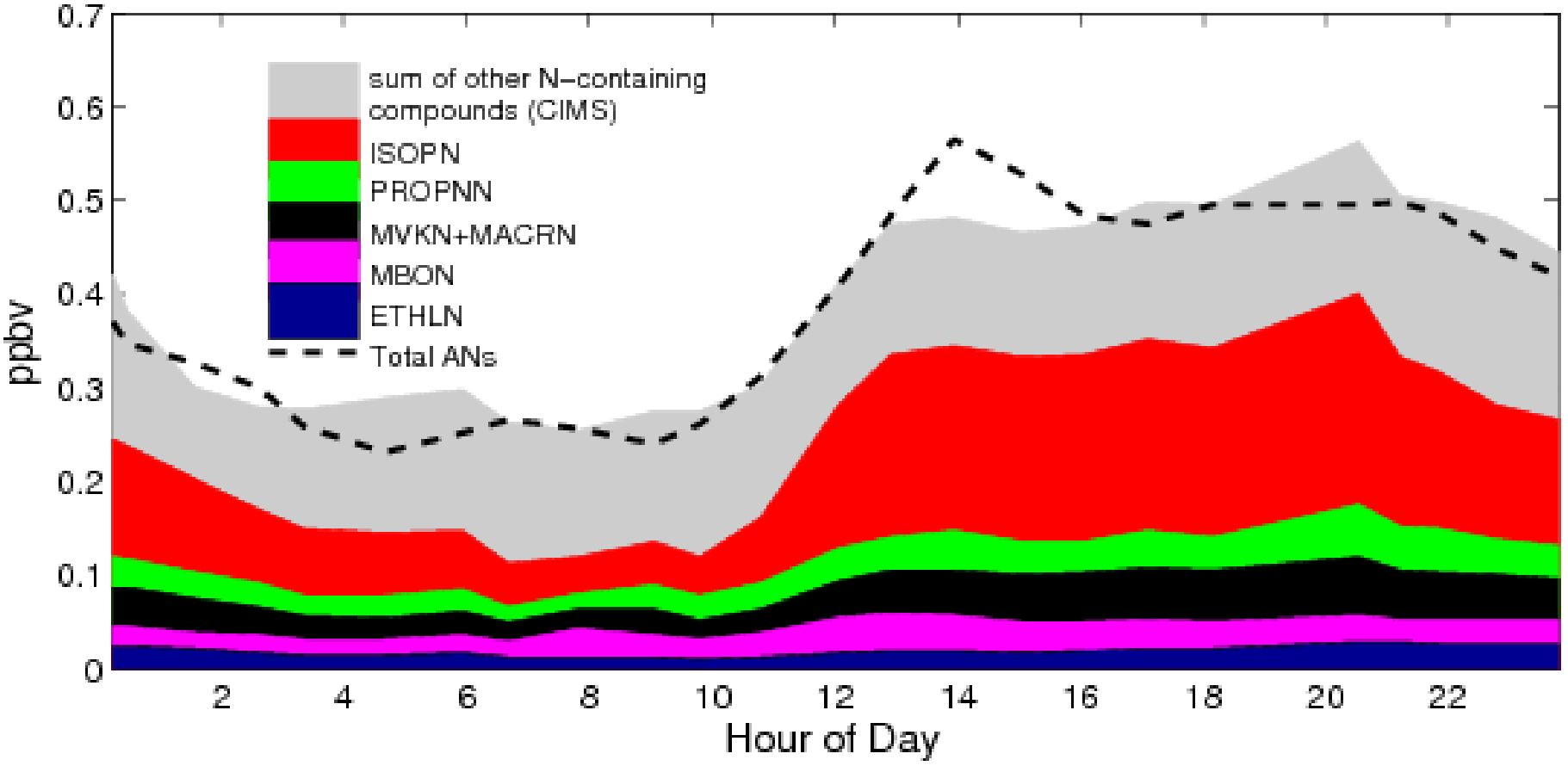
E-4-OH-1-ONO$_2$



Murphy et al.
ACP 2006

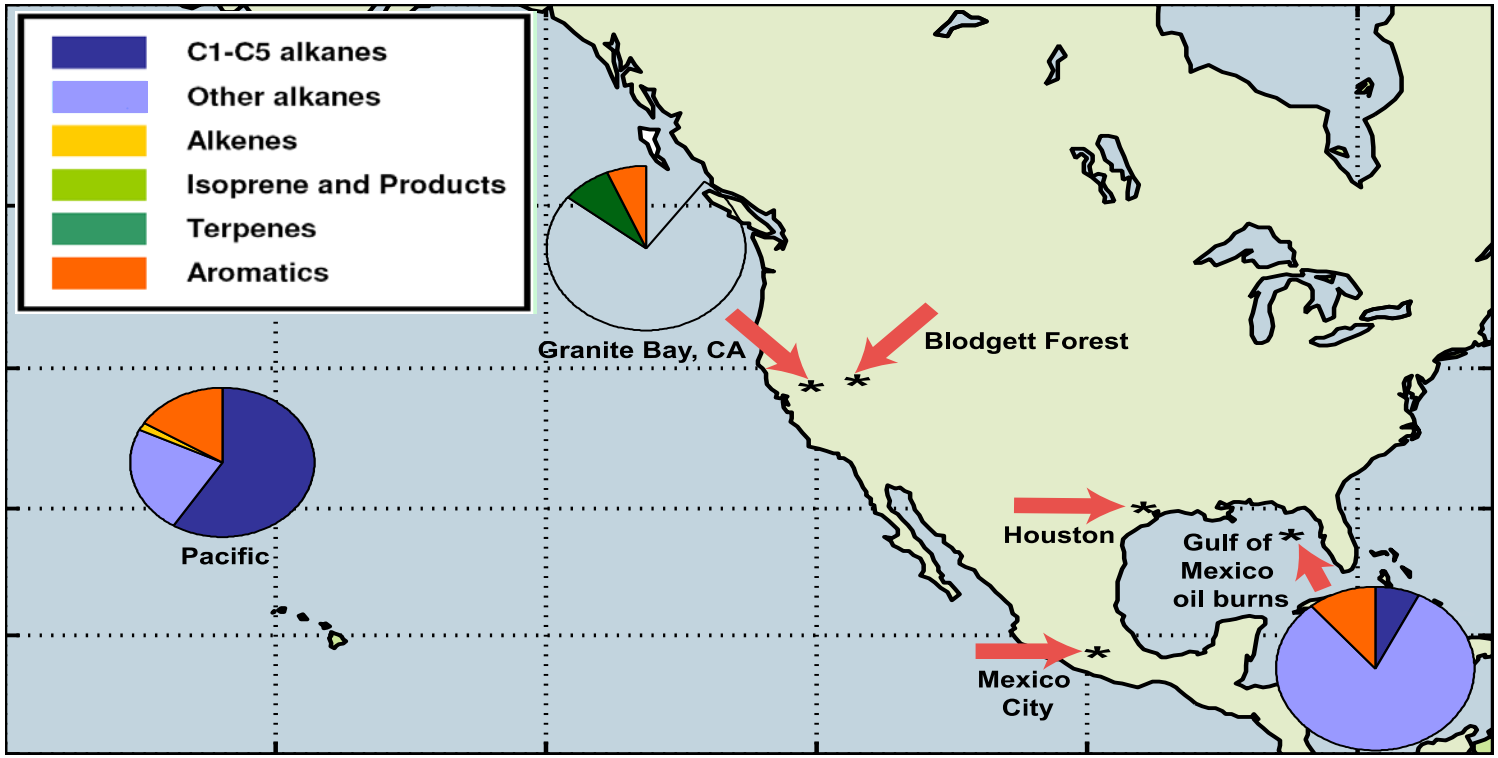
Big Hill

10 years later a comparison to an instrument capable of measuring relevant molecules at UC-BFRS (BEARPEX)



M. Beaver, et al. Atmos. Chem. Phys. 2012

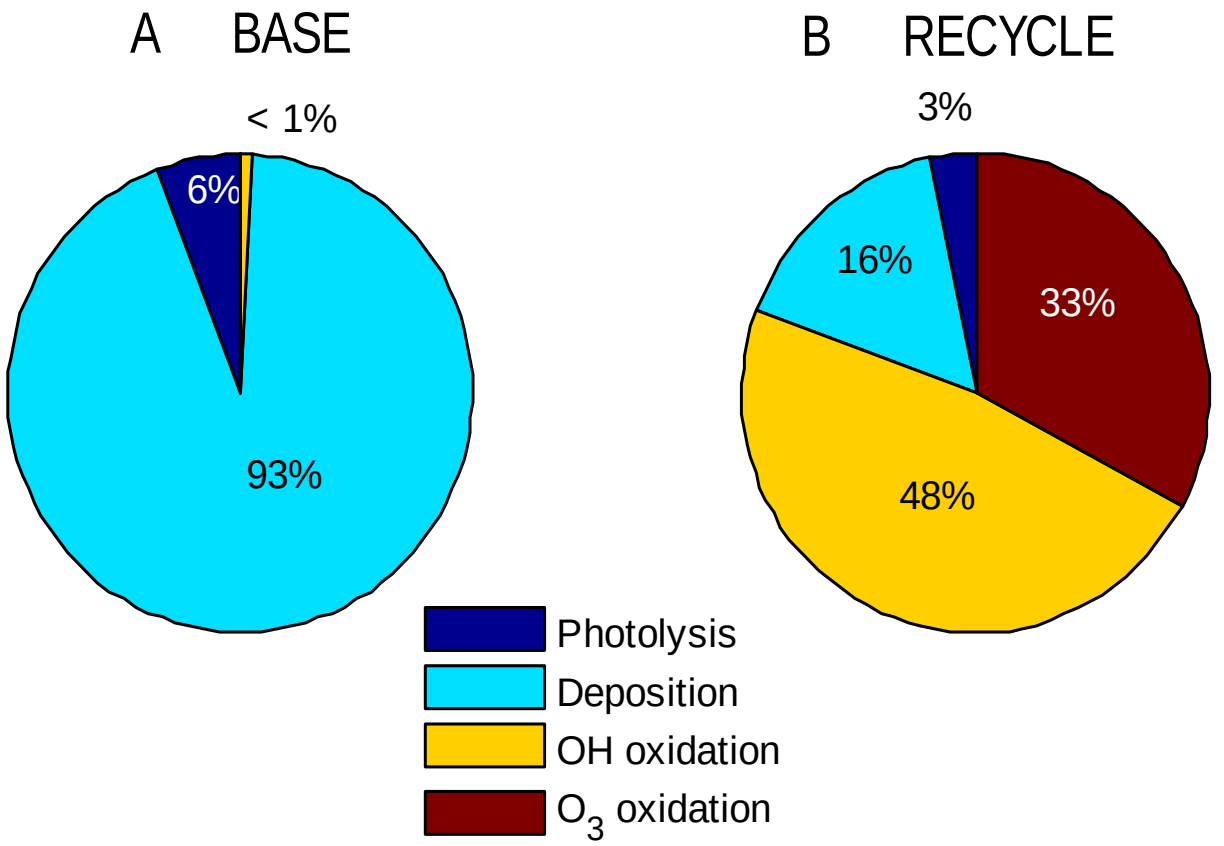
Local Production (w/o transport)



Perring, Pusede and Cohen, Chemical Reviews, 2013

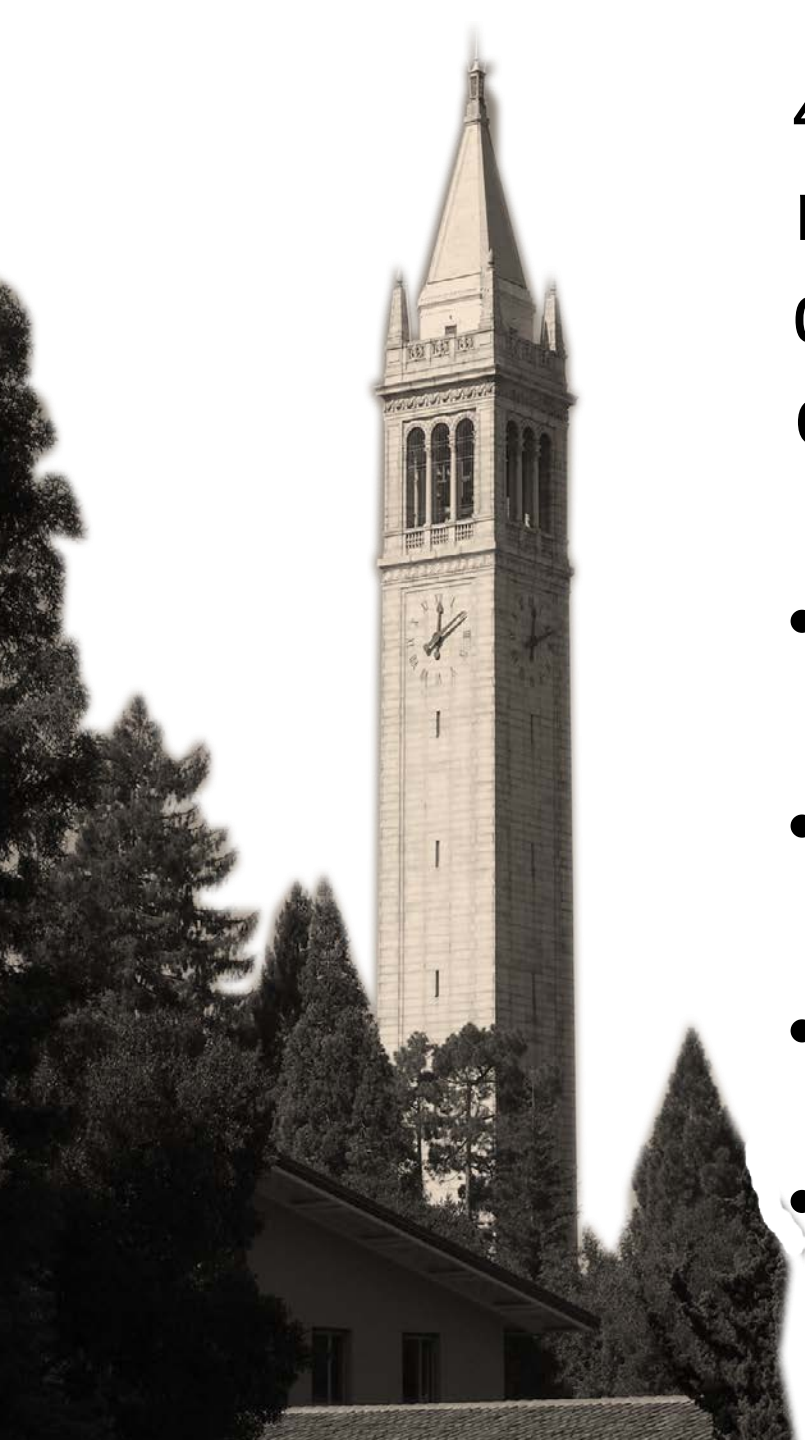
Monoterpene nitrate deposition vs. chemistry

Browne et al 2012, 2013 ACP



WRF Standard Chemistry

WRF Our guess at better chemistry

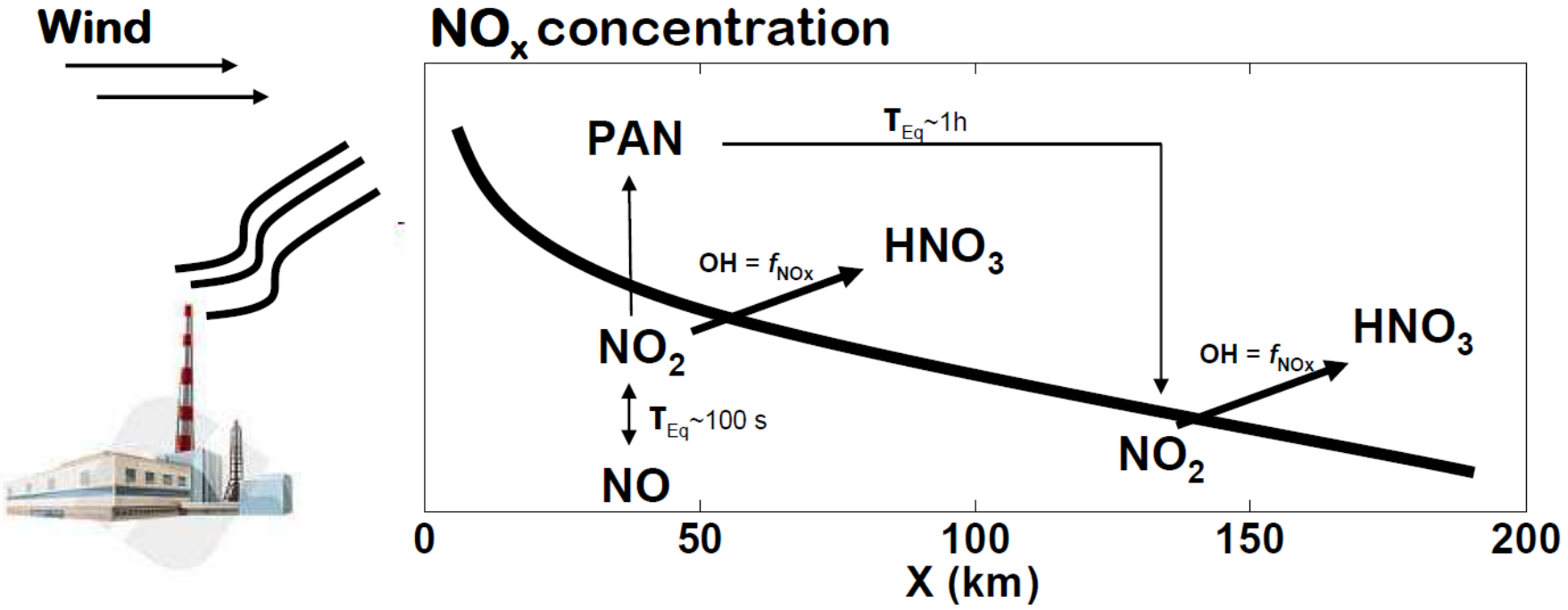


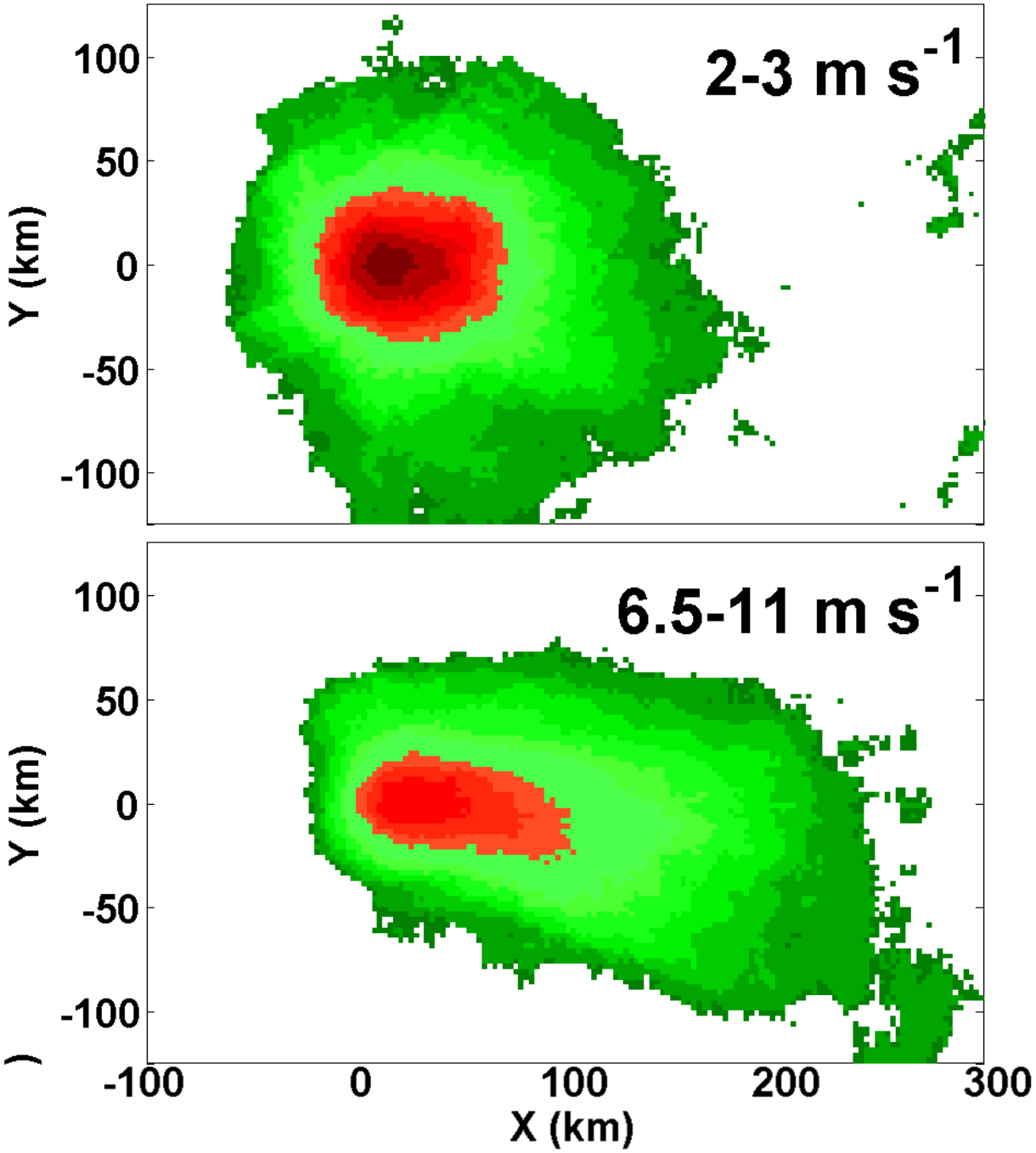
4 strategies toward a mechanistic description of the N-cycle

- Space based trends
- Eddy fluxes
- Aerosol $RONO_2$
- Fires and soils from space

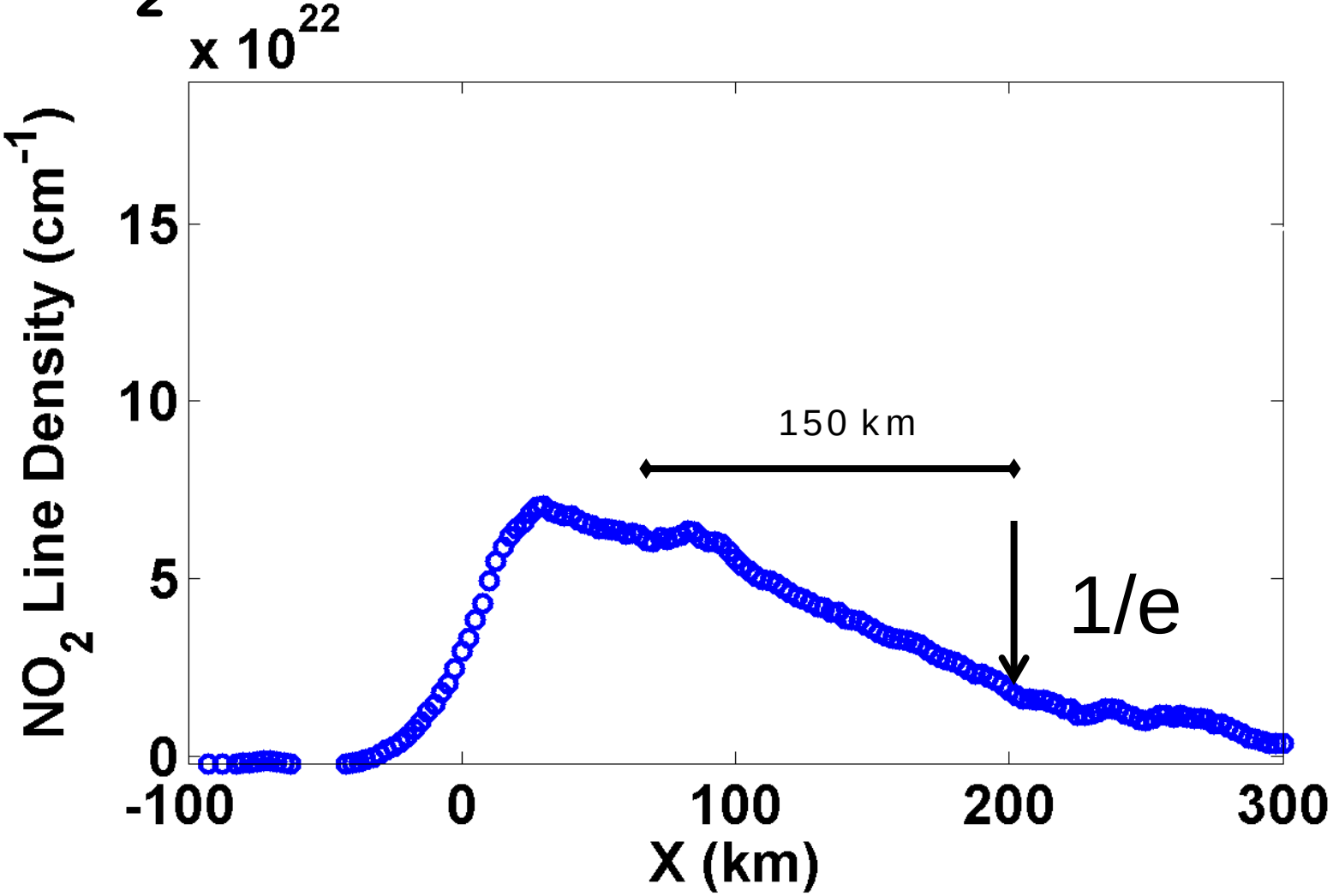
4 strategies toward a mechanistic description of the N-cycle

- Space based trends in emissions
- Eddy fluxes
- Aerosol $RONO_2$
- Fires and soils from space


Wind
NOx concentration
PAN
TEq~1h
HNO3
OH = fNOx
NO2
HNO3
OH = fNOx
TEq~100 s
NO2
NO
0
50
100
150
200
X (km)

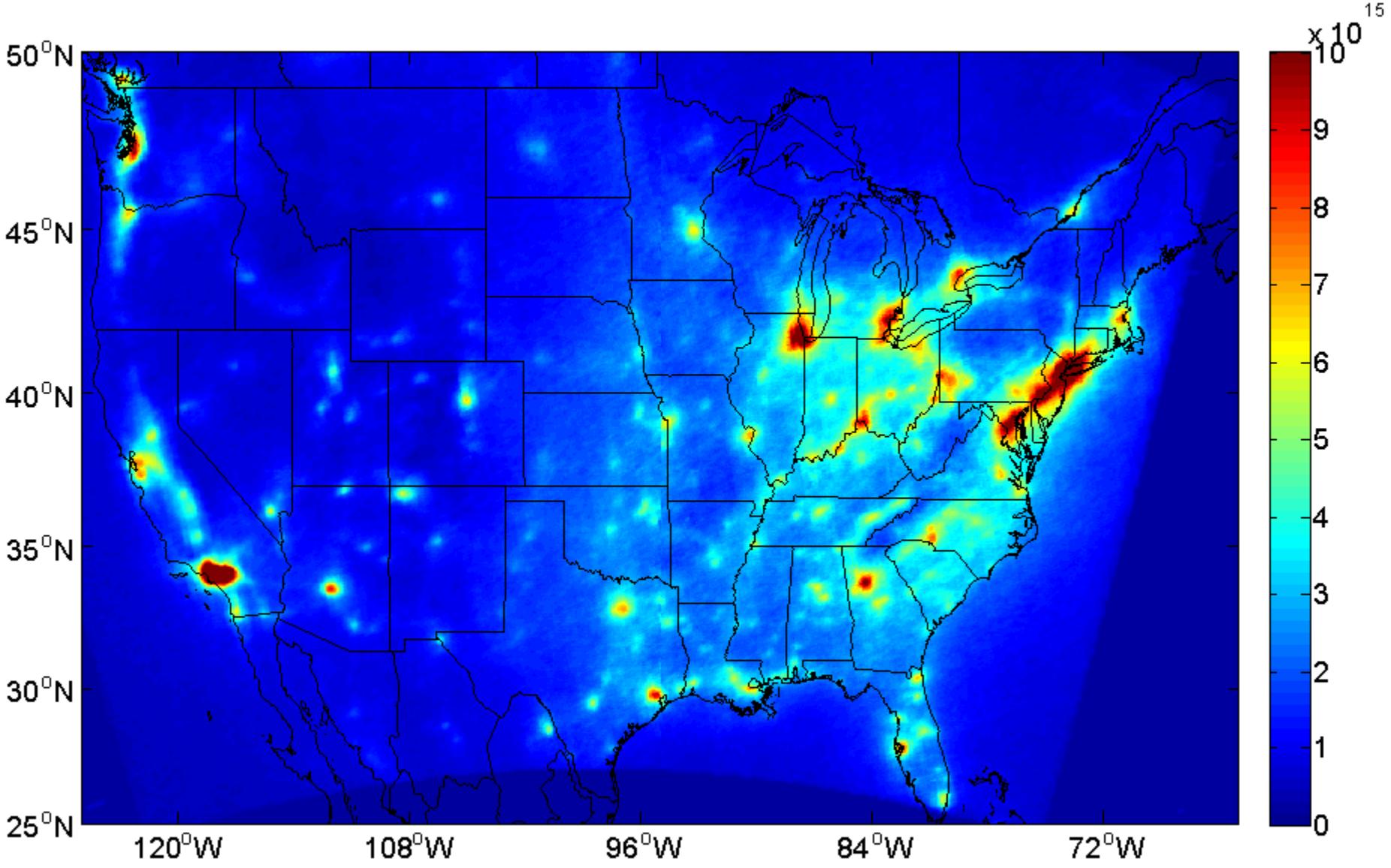

2-3 m s-1
6.5-11 m s-1
100
50
0
-50
-100
Y (km)
-100
0
100
200
300
X (km)

The NO_2 lifetime

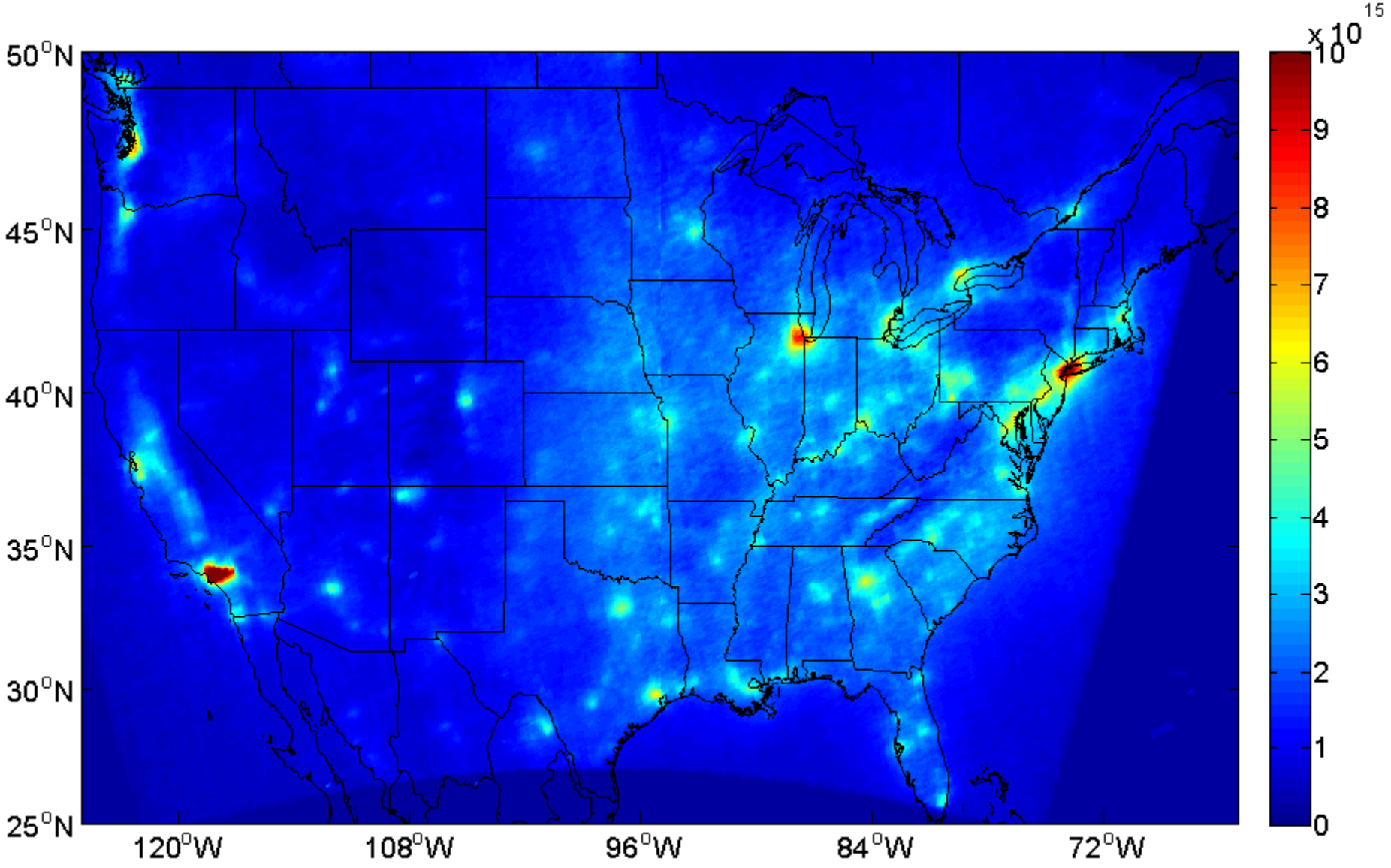


L Valin et al., *GRL 2013*

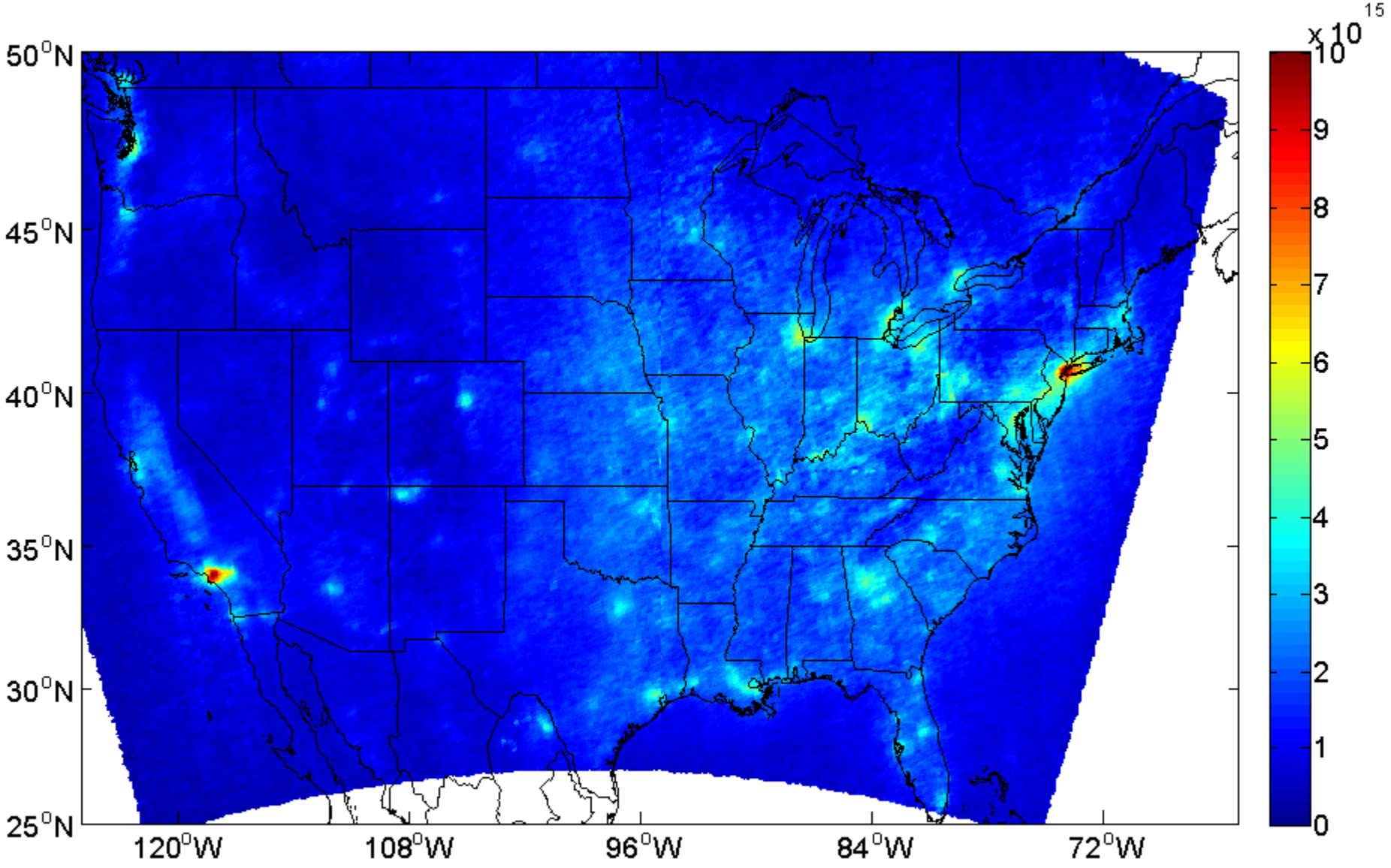
Trends in the U.S. and Canada


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

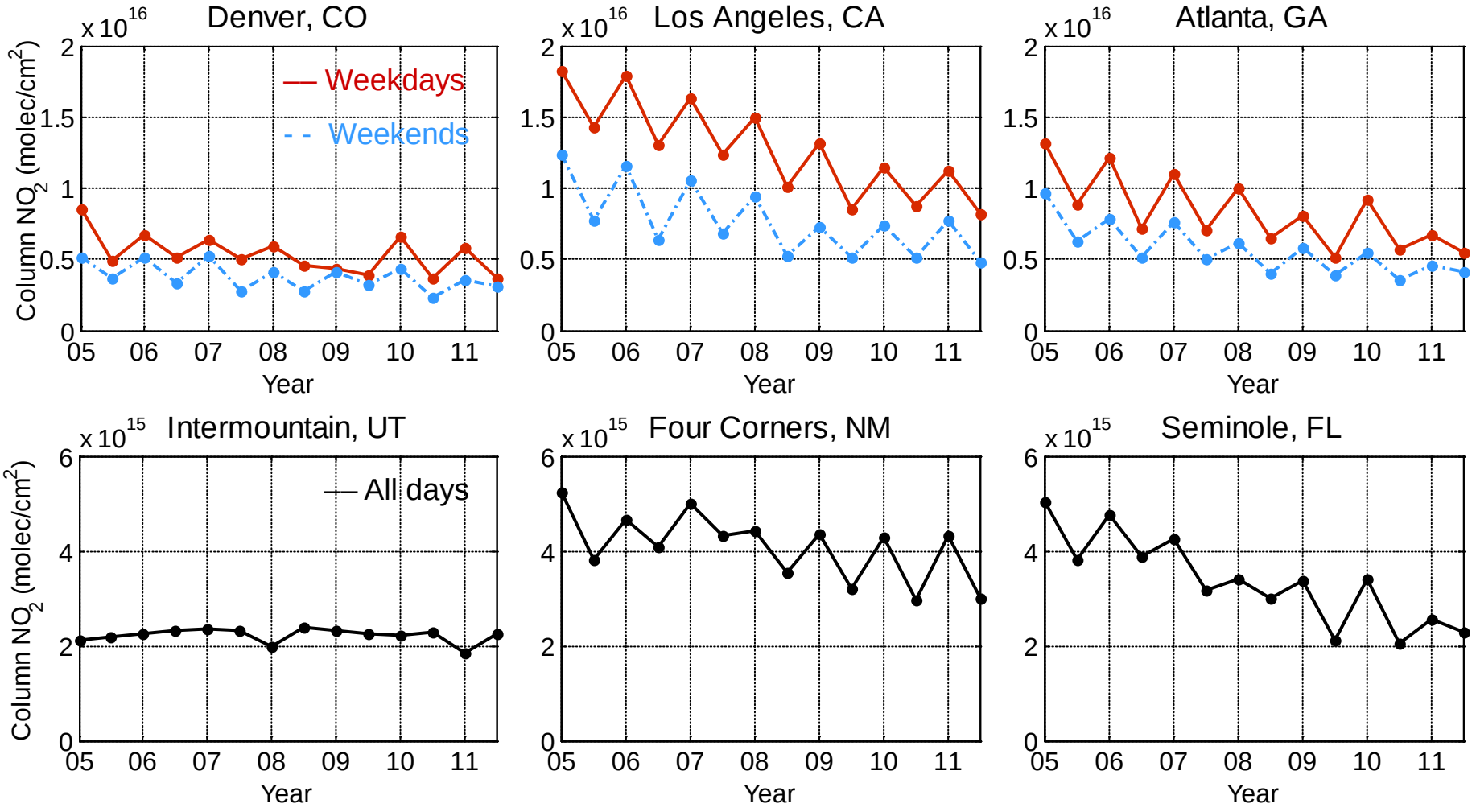

50°N
45°N
40°N
35°N
30°N
25°N
120°W
108°W
96°W
84°W
72°W
x 10^15
10
9
8
7
6
5
4
3
2
1
0

Summer 2011



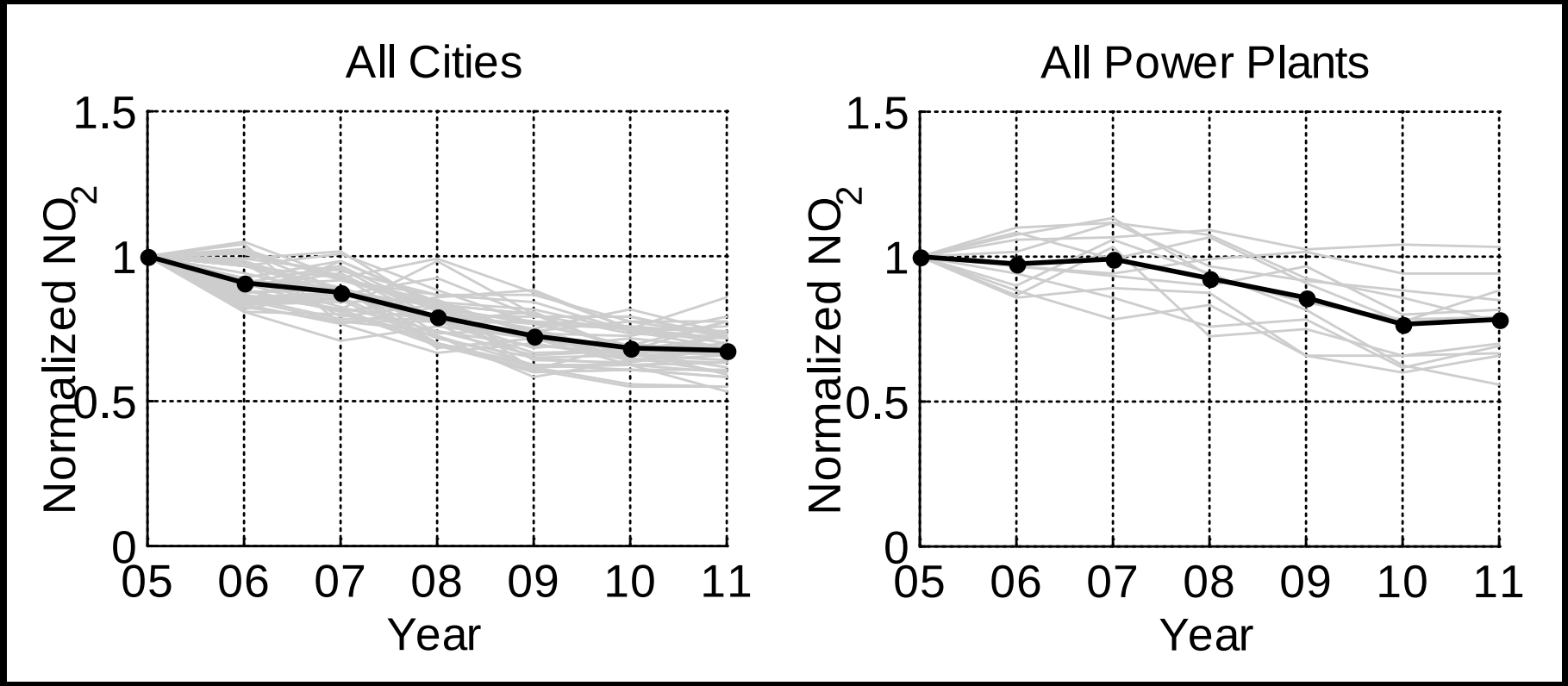
Weekend 2011

Trends for select cities and power plants



Russell et al., ACP 2012

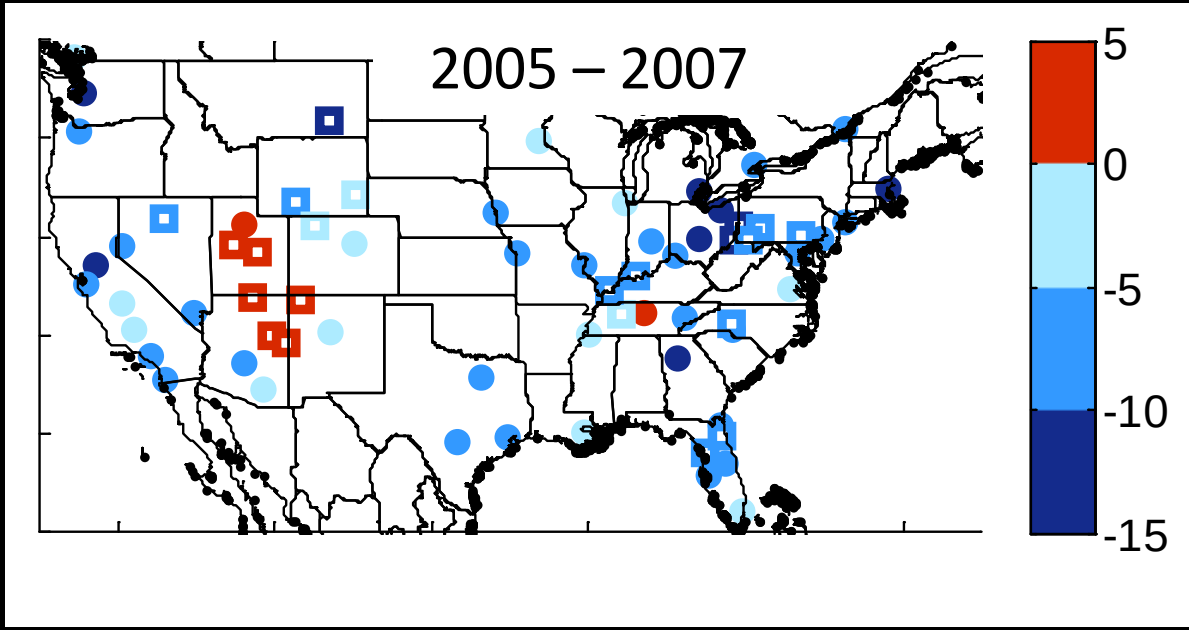
Trends in cities are similar while trends at power plants are more variable



47 cities, 23 power plants!

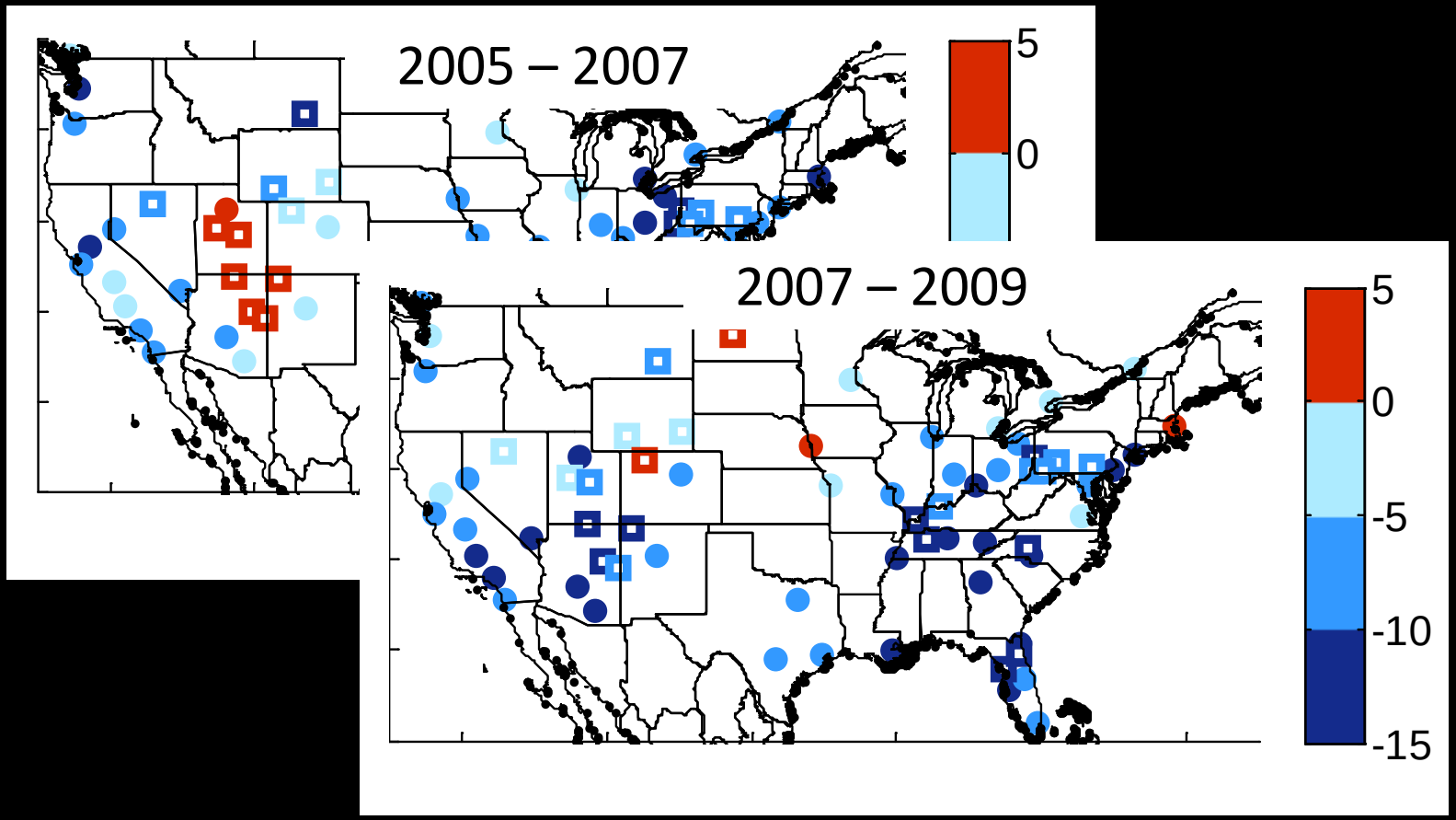
Russell et al., ACP 2012

The impact of the economic recession on emissions is observed by OMI



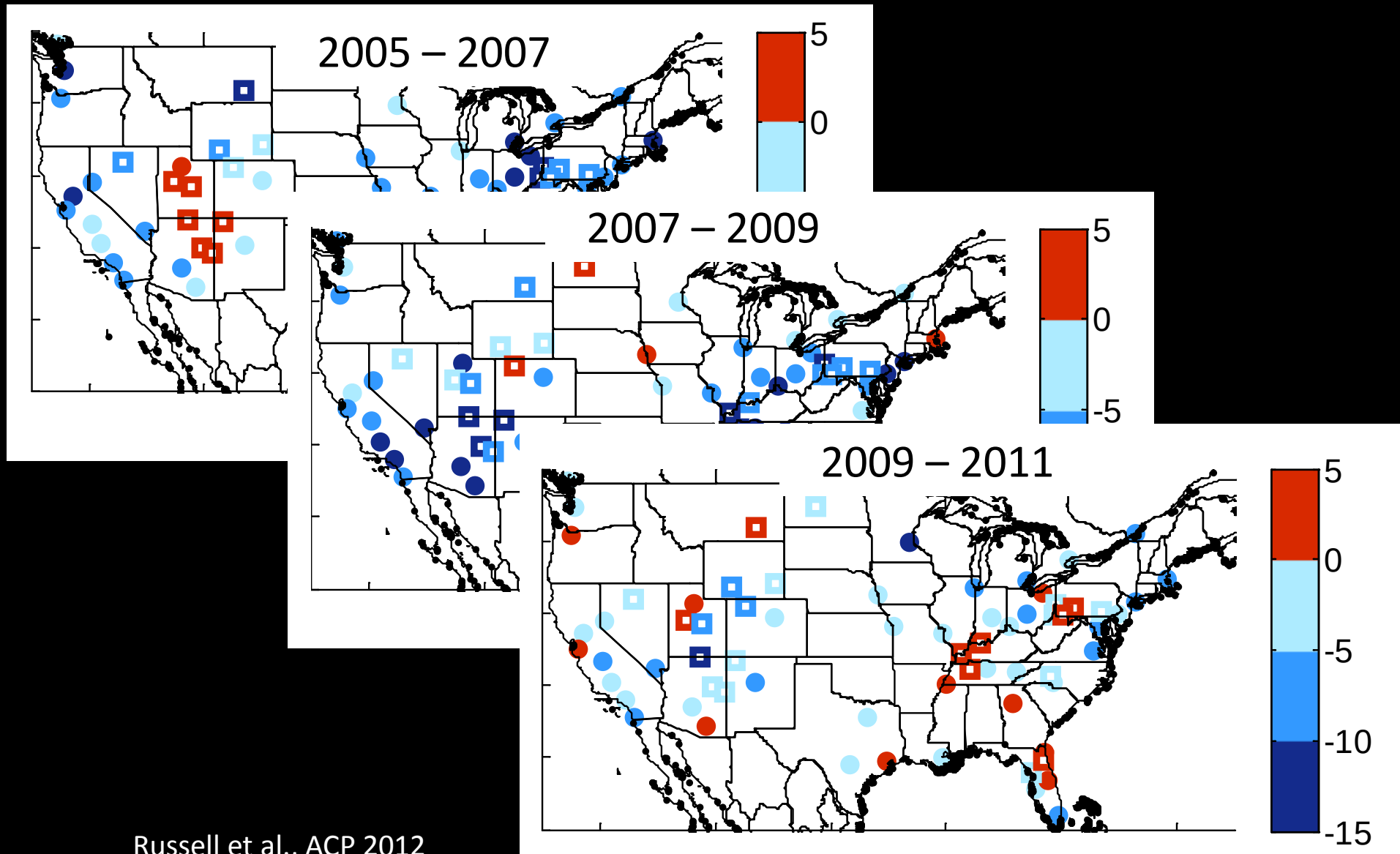
Russell et al., ACP 2012

The impact of the economic recession on emissions is observed by OMI



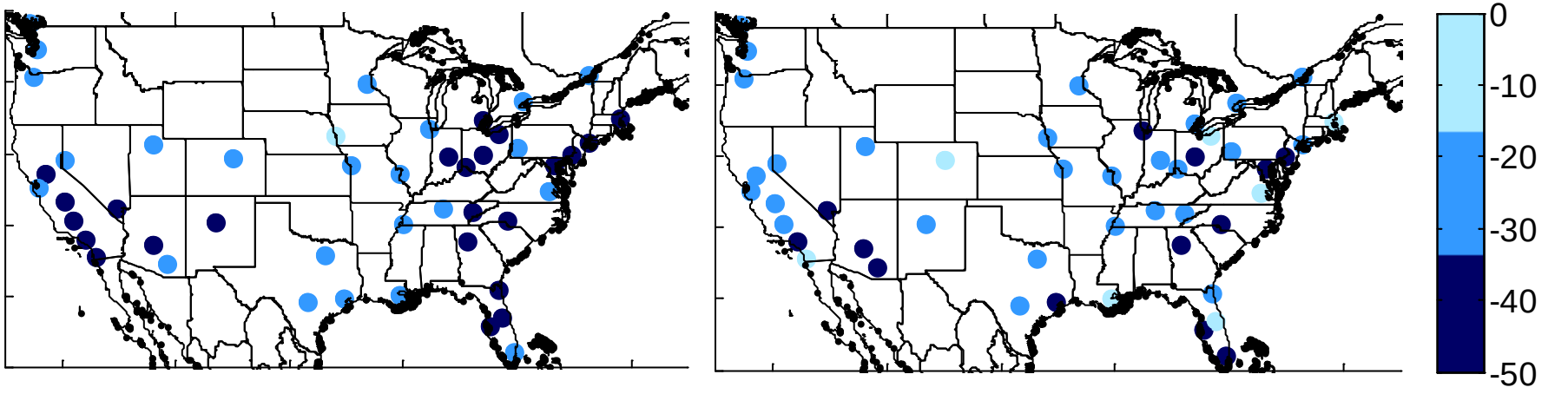
Russell et al., ACP 2012

The impact of the economic recession on emissions is observed by OMI



Russell et al., ACP 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., ACP 2012

NO_x Trends From Space

Catalytic convertors on automobiles and controls on power plants are an extraordinary success at reducing NO_x and organics.

Analysis of space-based observations 2005–2011 trends for cities and power plants in the US show how improved vehicle technology and the economic downturn have influenced emissions.

We also looked at some background locations and observed increasing trends—oil and gas production? Climate change? …

4 strategies toward a mechanistic description of the N-cycle

- Space based trends in emissions
- Eddy fluxes
- Aerosol $RONO_2$
- Fires and soils from space


Kyung-Eun Min
now a postdoc at NOAA
ACP, 2012, ACPD 2013

Deposition—Standard thinking

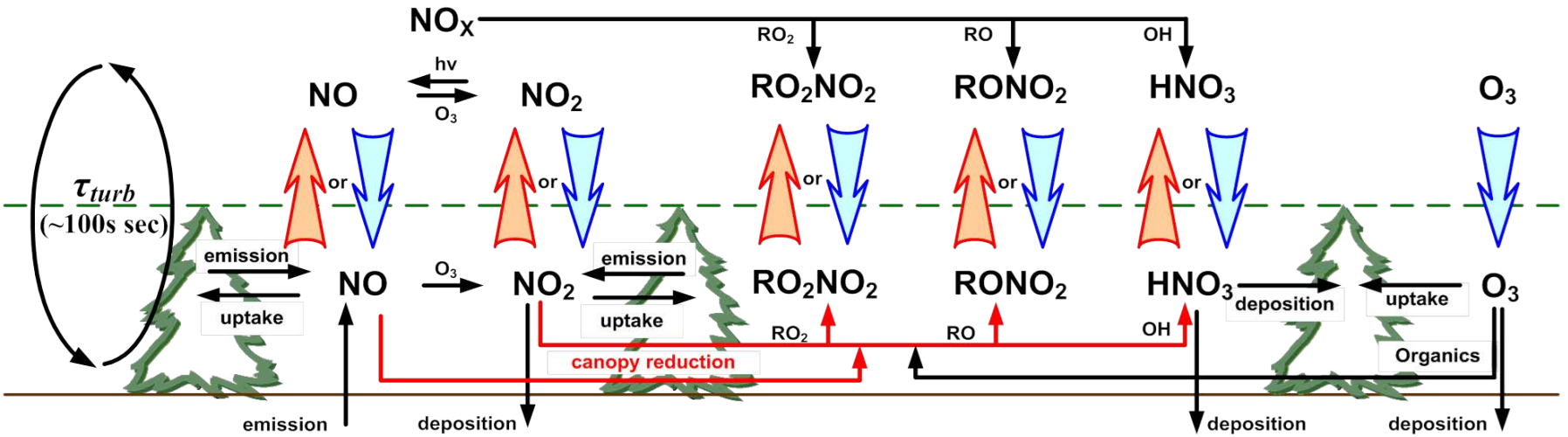
$NO_2 + OH \rightarrow HNO_3$

$HNO_3 \rightarrow HNO_3$

wet and dry deposition

both as gas and particle

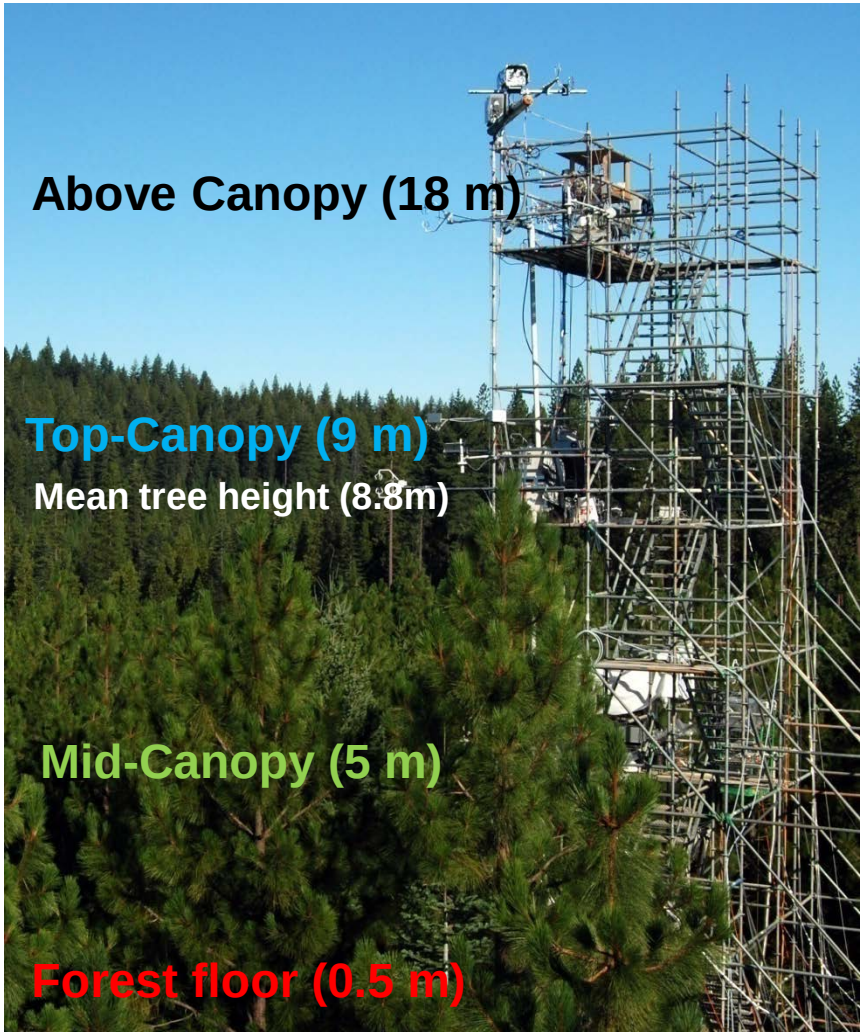
Deposition

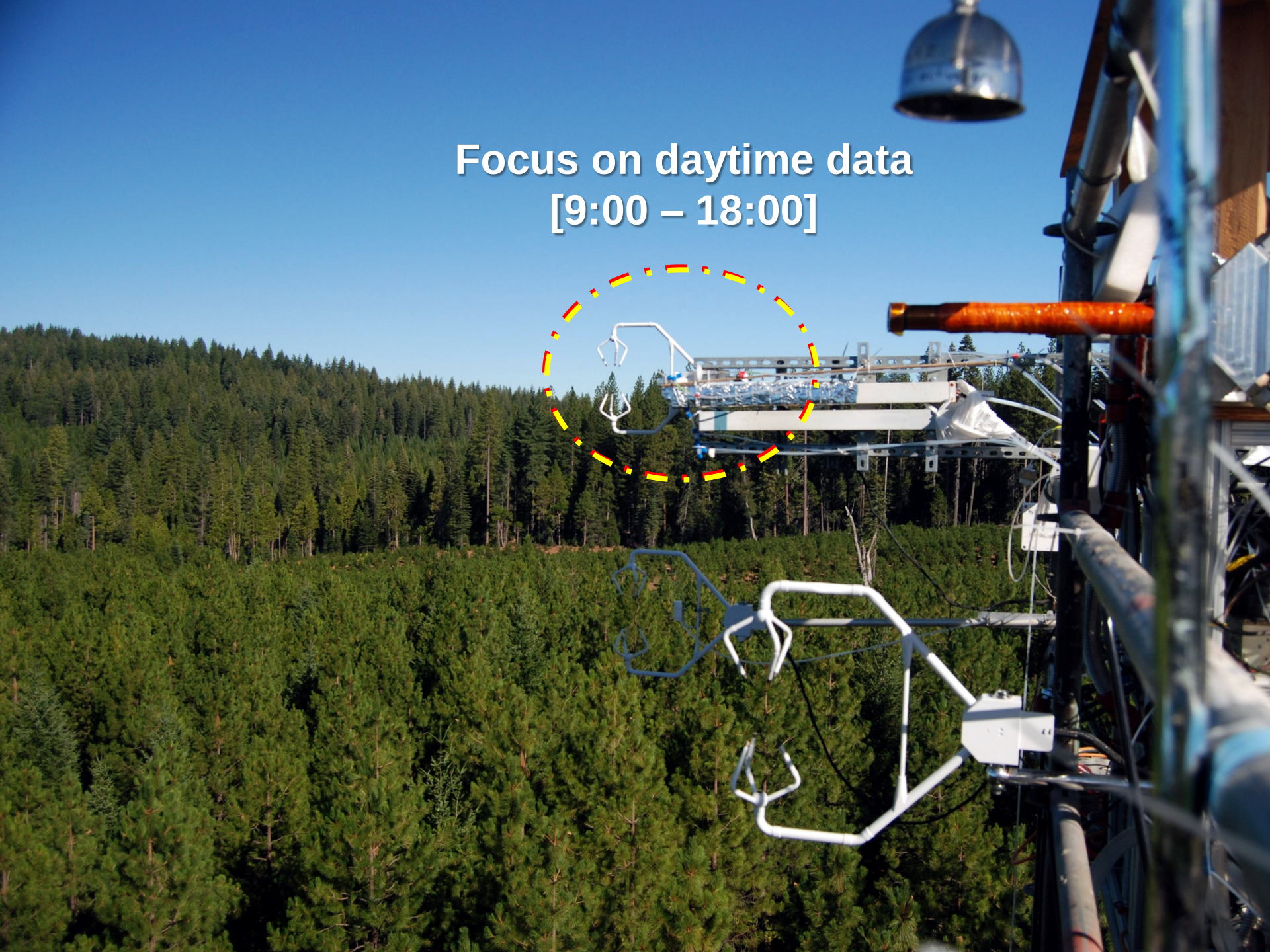

NOX
RO2
RO
OH
hv
O3
NO
NO2
RO2NO2
RONO2
HNO3
O3
τturb
(~100s sec)
or
emission
uptake
NO
O3
NO2
RO2NO2
RONO2
HNO3
deposition
uptake
O3
RO2
RO
OH
canopy reduction
Organics
emission
deposition
deposition
deposition

BEARPEX 2009

(Biosphere Effects on AeRosol & Photochemistry Experiment)

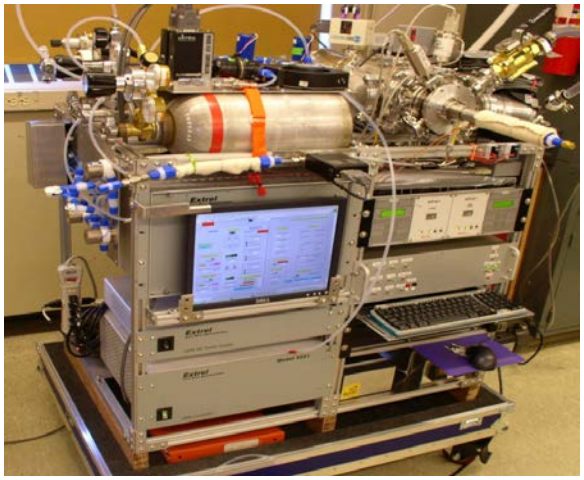
June 15th – July 31st, 2009




Focus on daytime data
[9:00 – 18:00]

Sonic Anemometer, 10Hz: 3D wind data

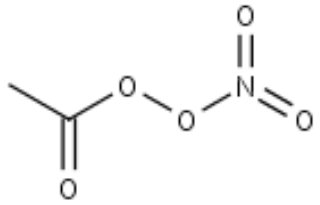
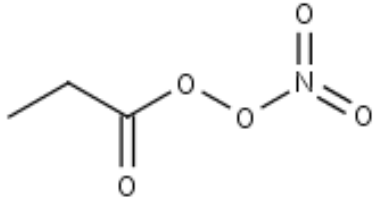
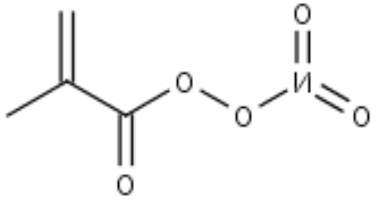
TD-LIF, 5Hz: NO_2, ∑ PN, ∑ AN, HNO_3
Cohen group, UC, Berkeley
Thermal Dissociation-Laser Induced Fluorescence



TD-CIMS, 3Hz: PAN, PPN, MPAN
Thornton group, UW
Thermal Dissociation-Chemical Ionization Mass Spectrometry

What is RO_2NO_2 ?

$$NO_2 + RO_2 \underset{\text{heat}}{\rightleftharpoons} RO_2NO_2$$

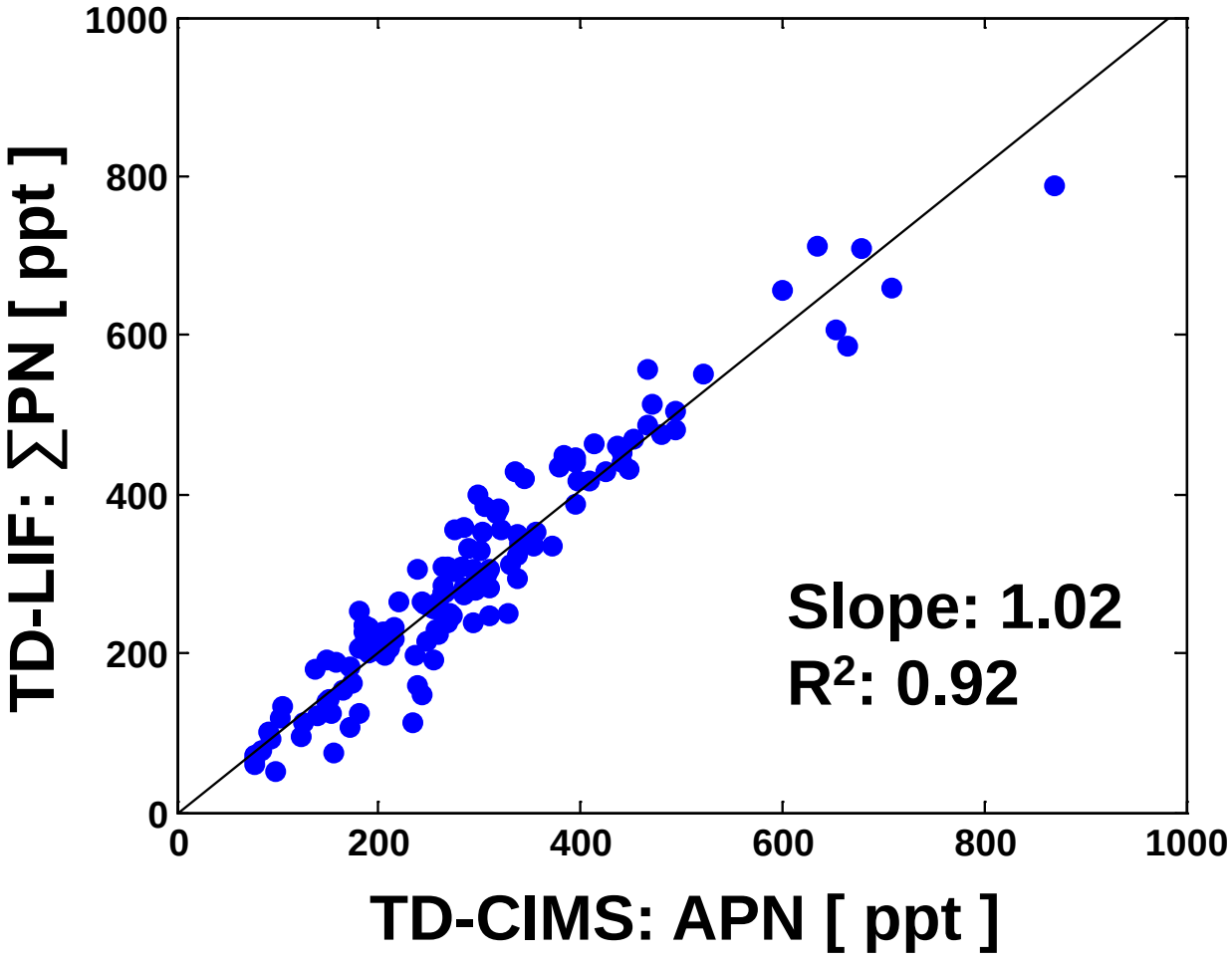
PAN	PPN	MPAN
$CH_3C(O)OONO_2$	$CH_3CH_2C(O)OONO_2$	$CH_3C(CH_2)C(O)OONO_2$
		

Definition

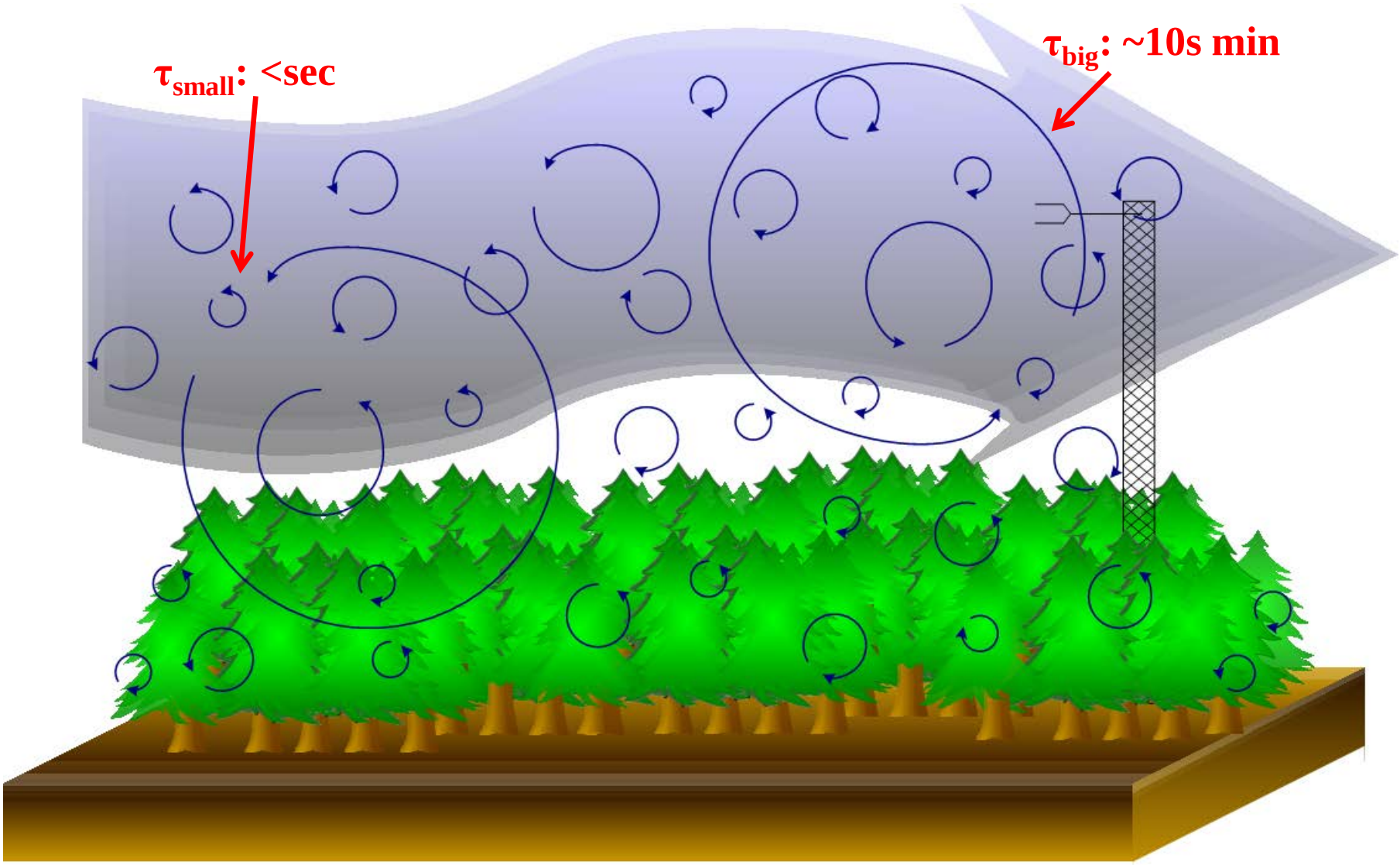
APN = PAN + PPN + MPAN

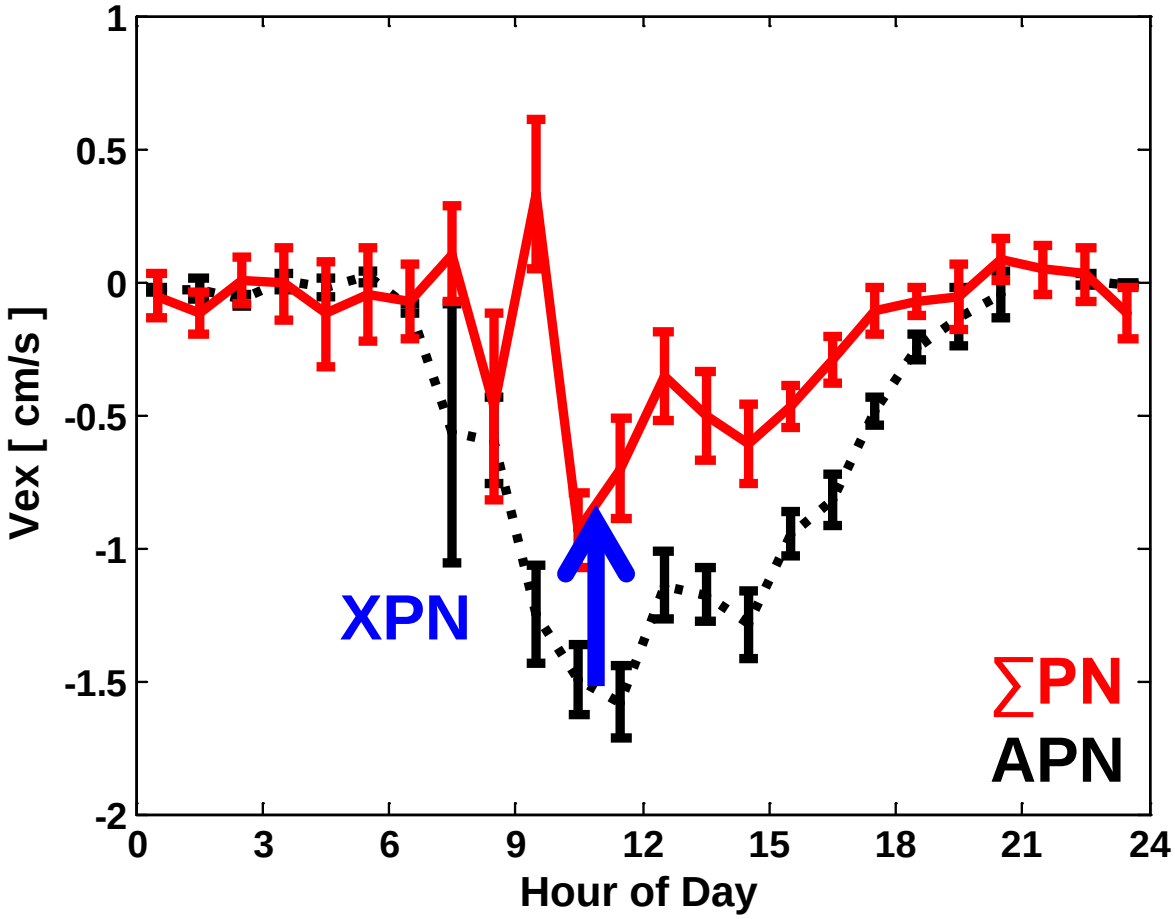
$\sum$PN = PAN + PPN + MPAN + • • •

∑PN ≈ APN [Wooldridge et al, 2010]



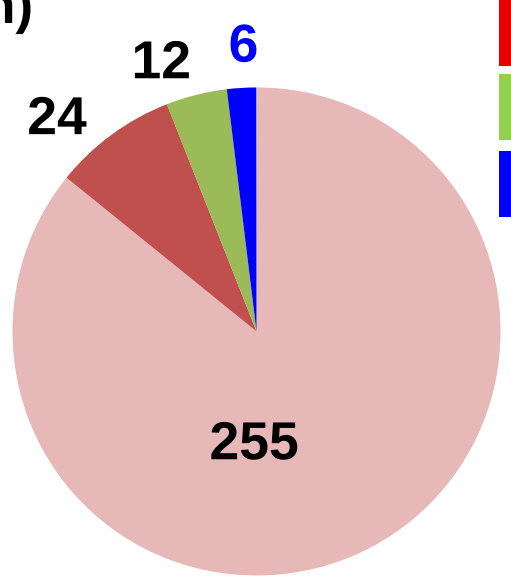
Eddy-Covariance method




1
0.5
0
-0.5
-1
-1.5
-2
Vex [cm/s]
0
3
6
9
12
15
18
21
24
Hour of Day
XPN
∑PN
APN

Above Canopy (18 m)

∑PN: 297ppt

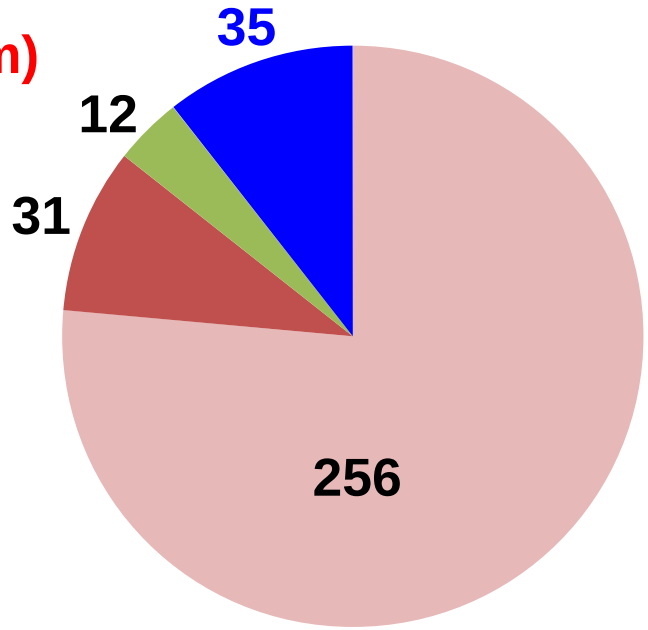


PAN
MPAN
PPN
XPN

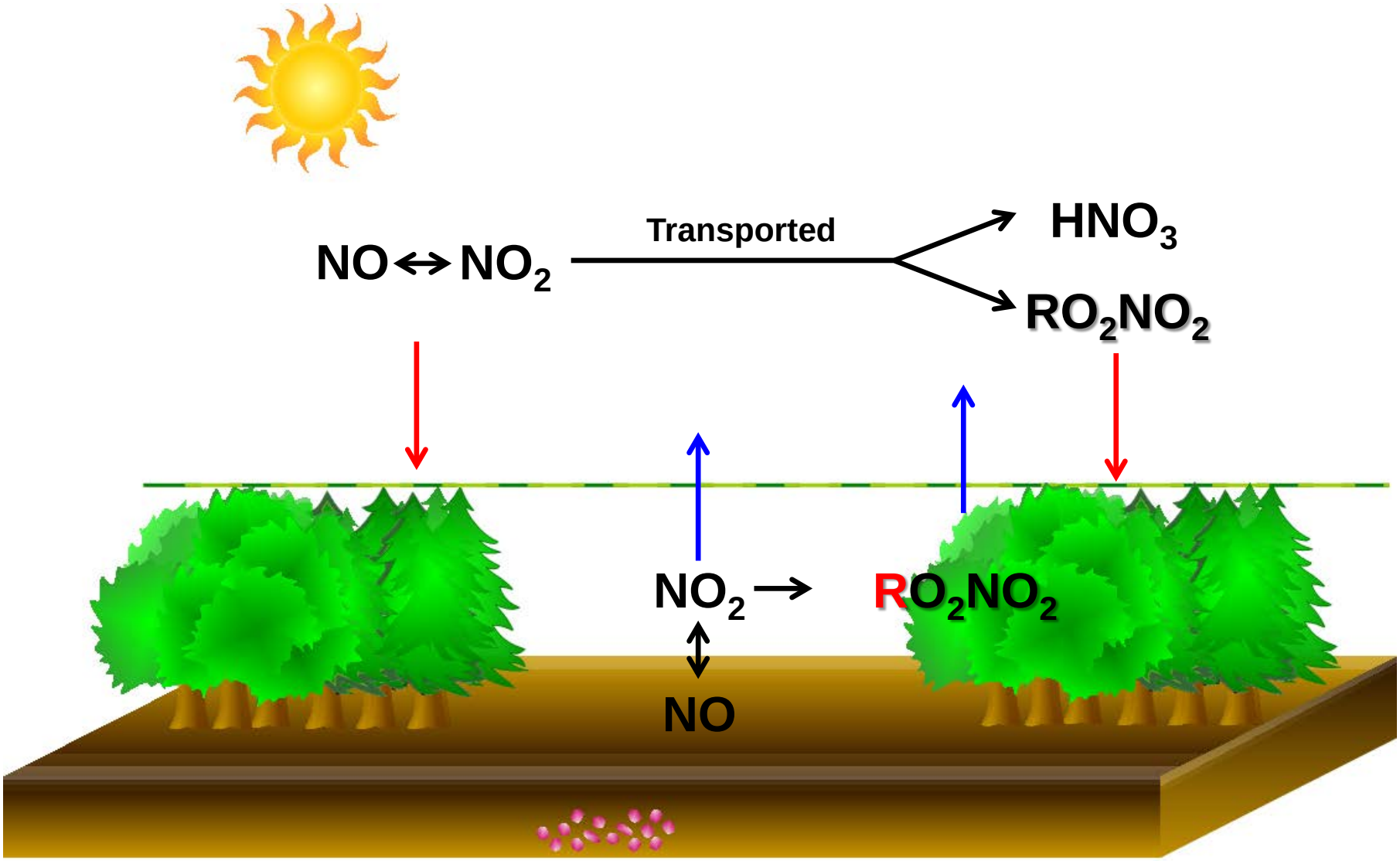
Unit: ppt

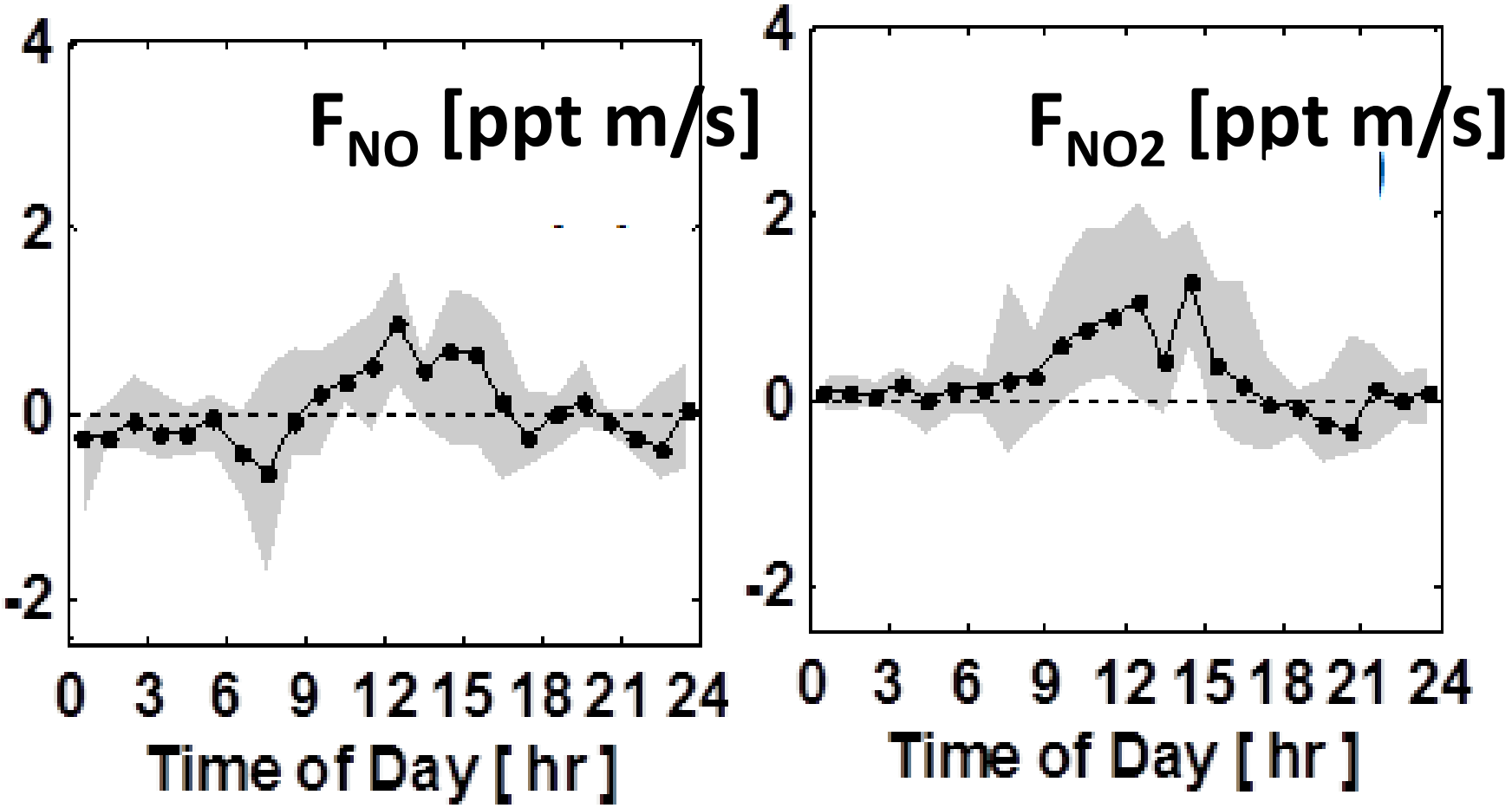
Forest floor (0.5 m)

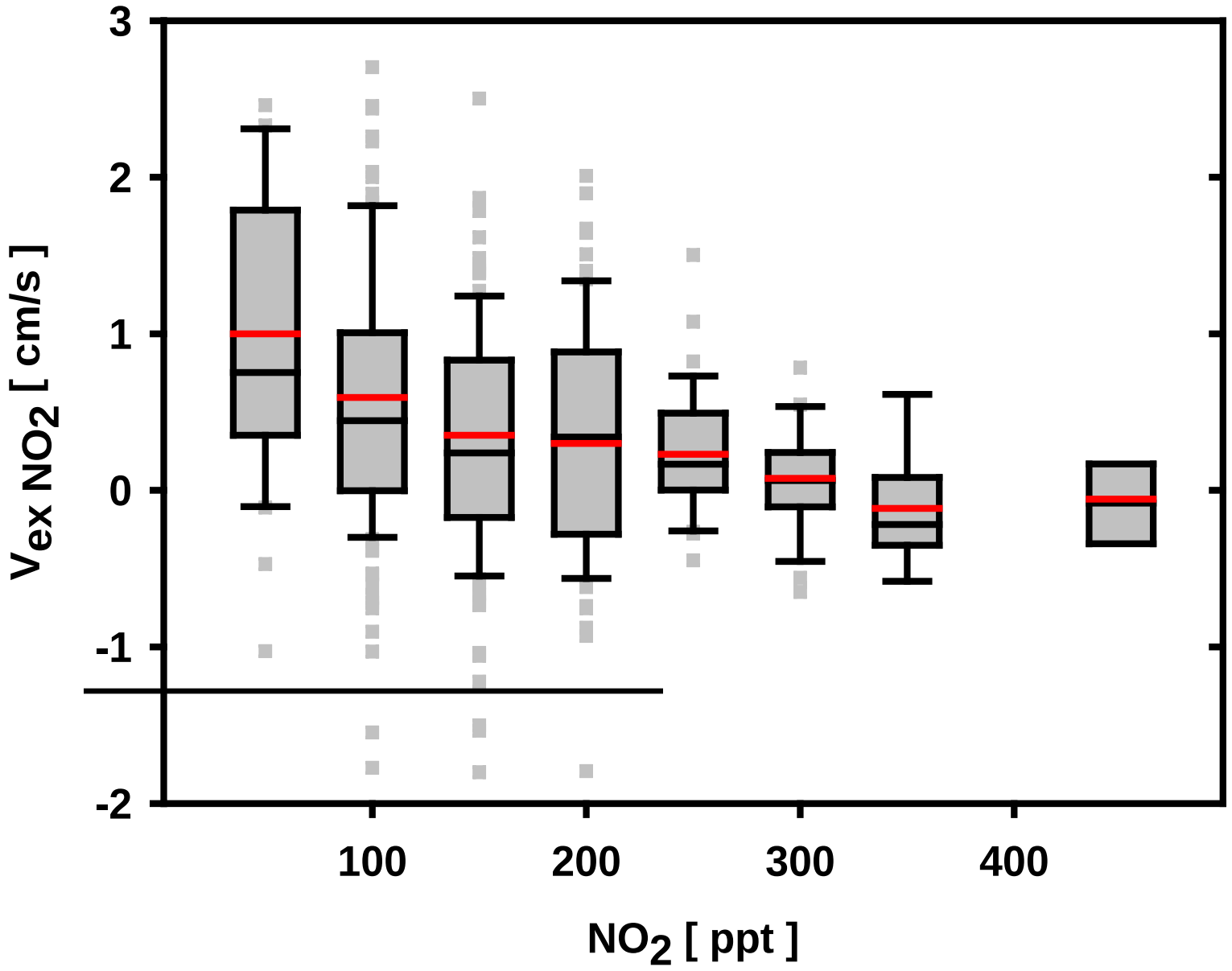
∑PN: 334 ppt

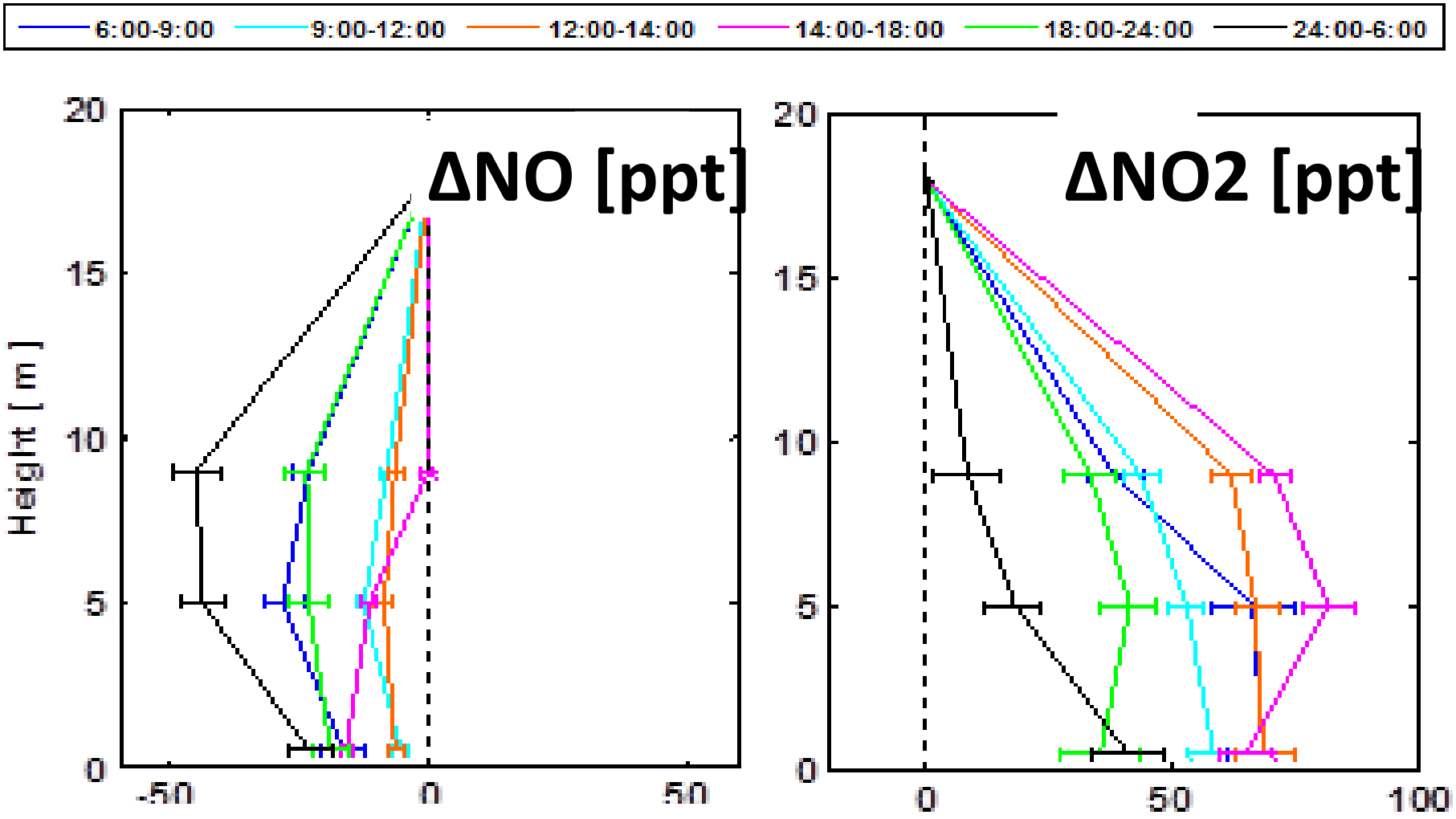


Unusual PN formation affects PN exchange rates




F_{NO} [ppt m/s]
F_{NO2} [ppt m/s]
4
2
0
-2
0 3 6 9 12 15 18 21 24
Time of Day [hr]


3
2
1
0
-1
-2
100
200
300
400
V_{ex} NO_2 [cm/s]
NO_2 [ppt]


6:00-9:00
9:00-12:00
12:00-14:00
14:00-18:00
18:00-24:00
24:00-6:00
ΔNO [ppt]
ΔNO2 [ppt]
Height [m]
20
15
10
5
0
-50
0
50
100

4 strategies toward a mechanistic description of the N-cycle

- Space based trends
- Eddy fluxes
- Aerosol $RONO_2$
- Fires and soils from space

Drew Rollins

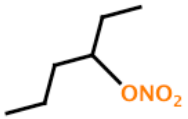
Rollins et al., Science Sept 7, 2012

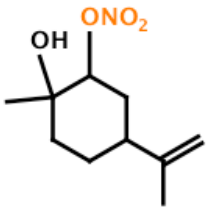
OH + NO

$RONO_2$ yields ≈ 0-30%

$RONO_2$

C* > 100 µg/m³





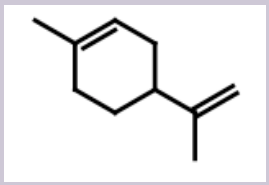
CONDENSED PHASE

$H_2O(l)$ $ROH + HNO_3$

$RONO_2$

H_2SO_4 $ROSO_3H + HNO_3$

NO_3



$RONO_2$ yields > 50%

OH

O_3

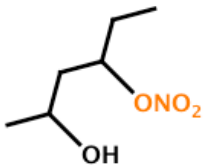
NO_3

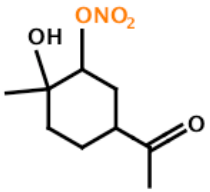
NO_x

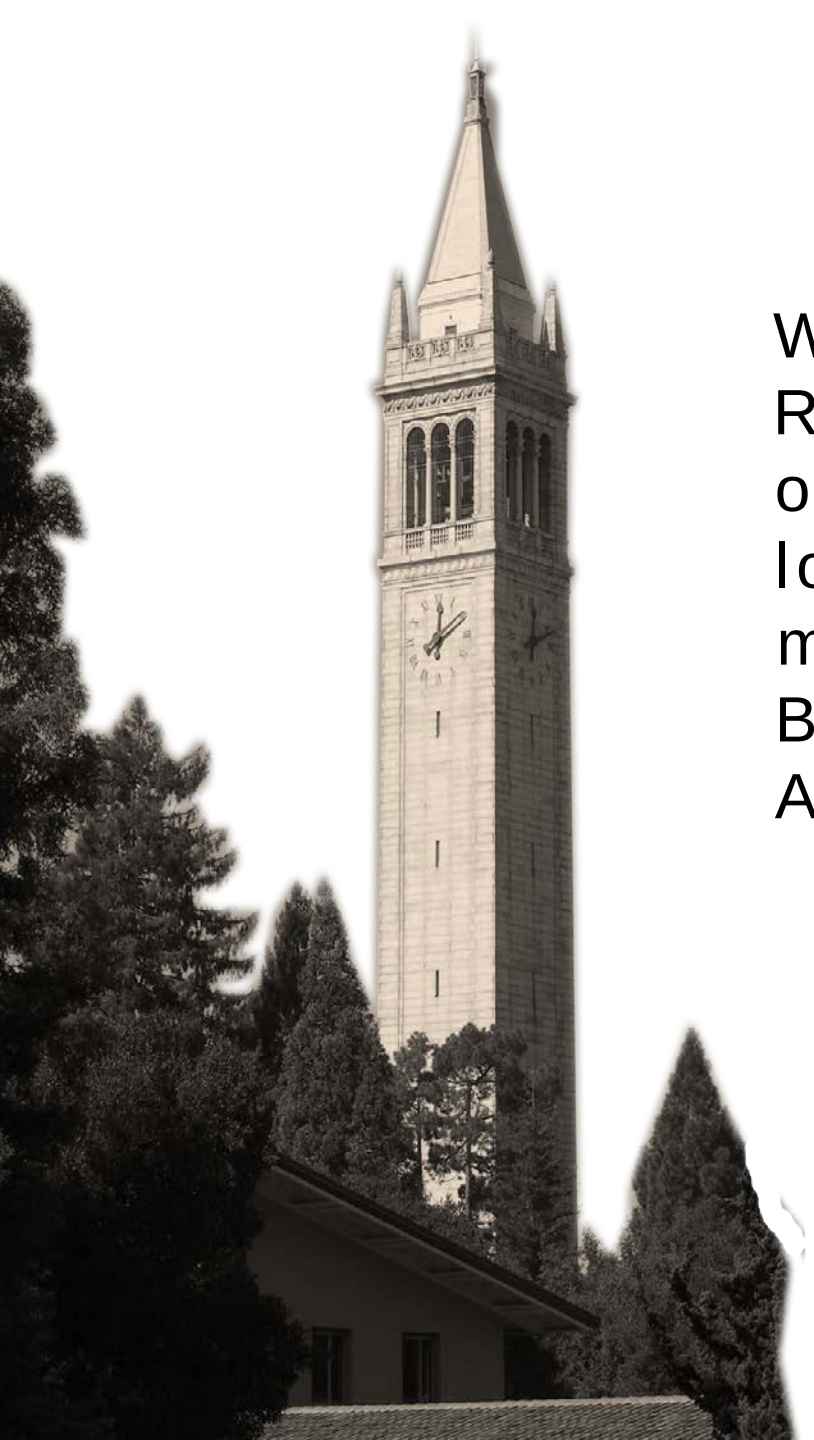
HNO_3

$RONO_2$

C* > 0.1 µg/m³

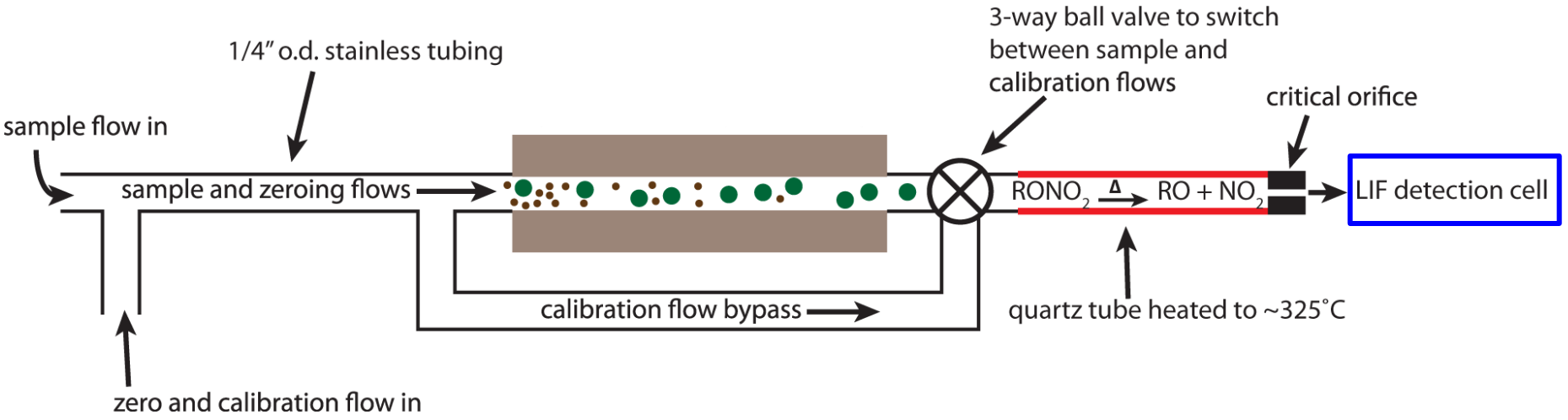


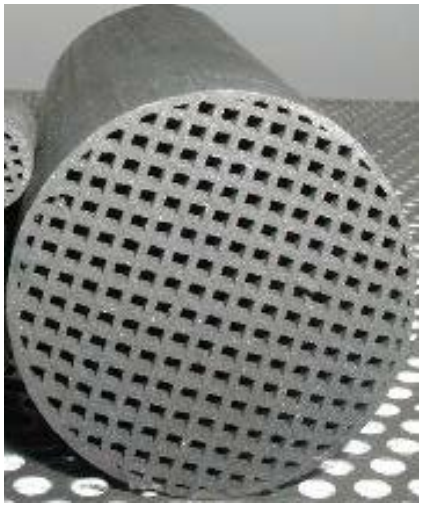




We observe that aerosol $RONO_2$ is a large fraction of SOA ~30% at the two locations where we have made observations—Bakersfield and rural Alabama

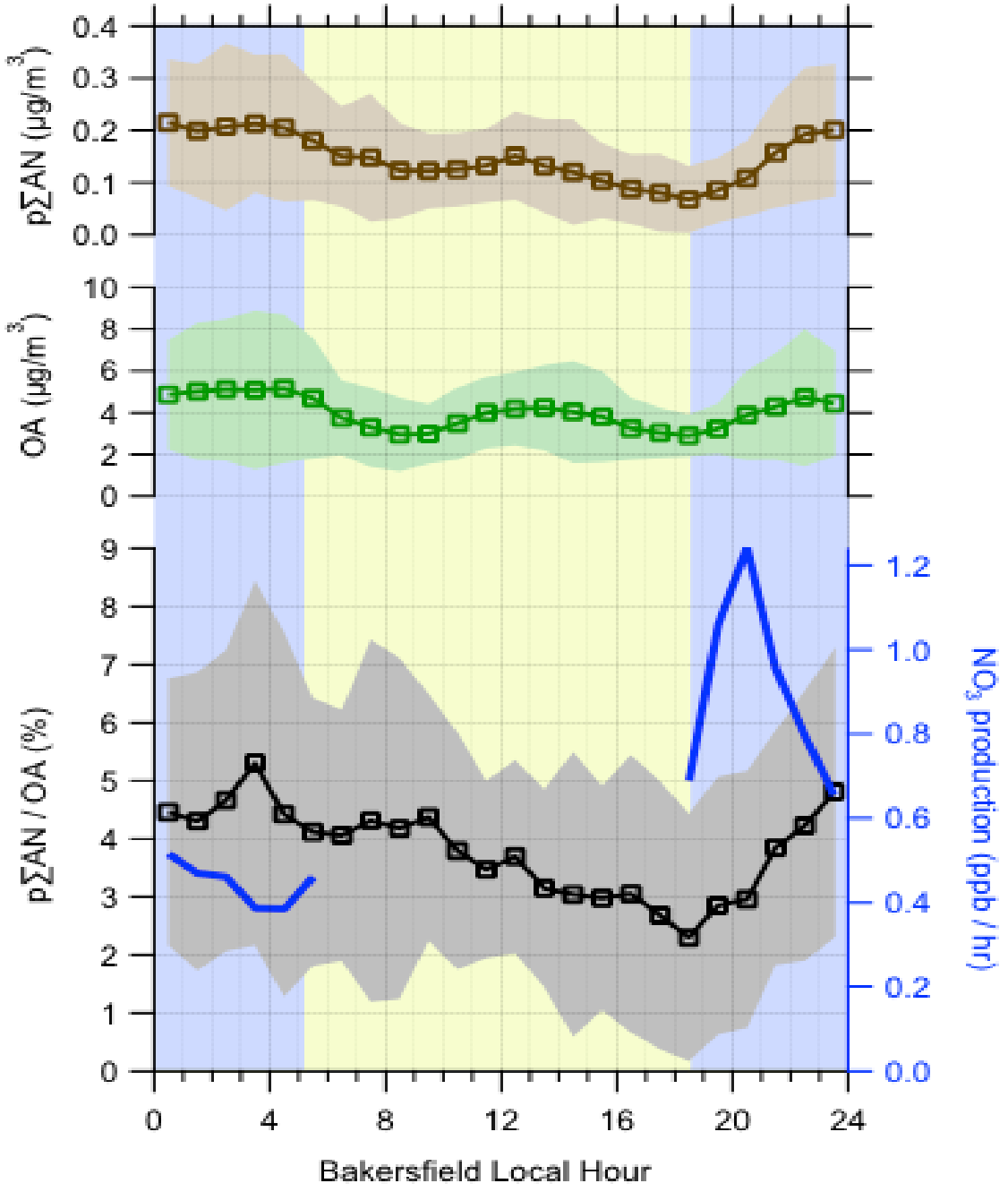
Thermal Dissociation Laser Induced Fluorescence (TD-LIF)





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

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



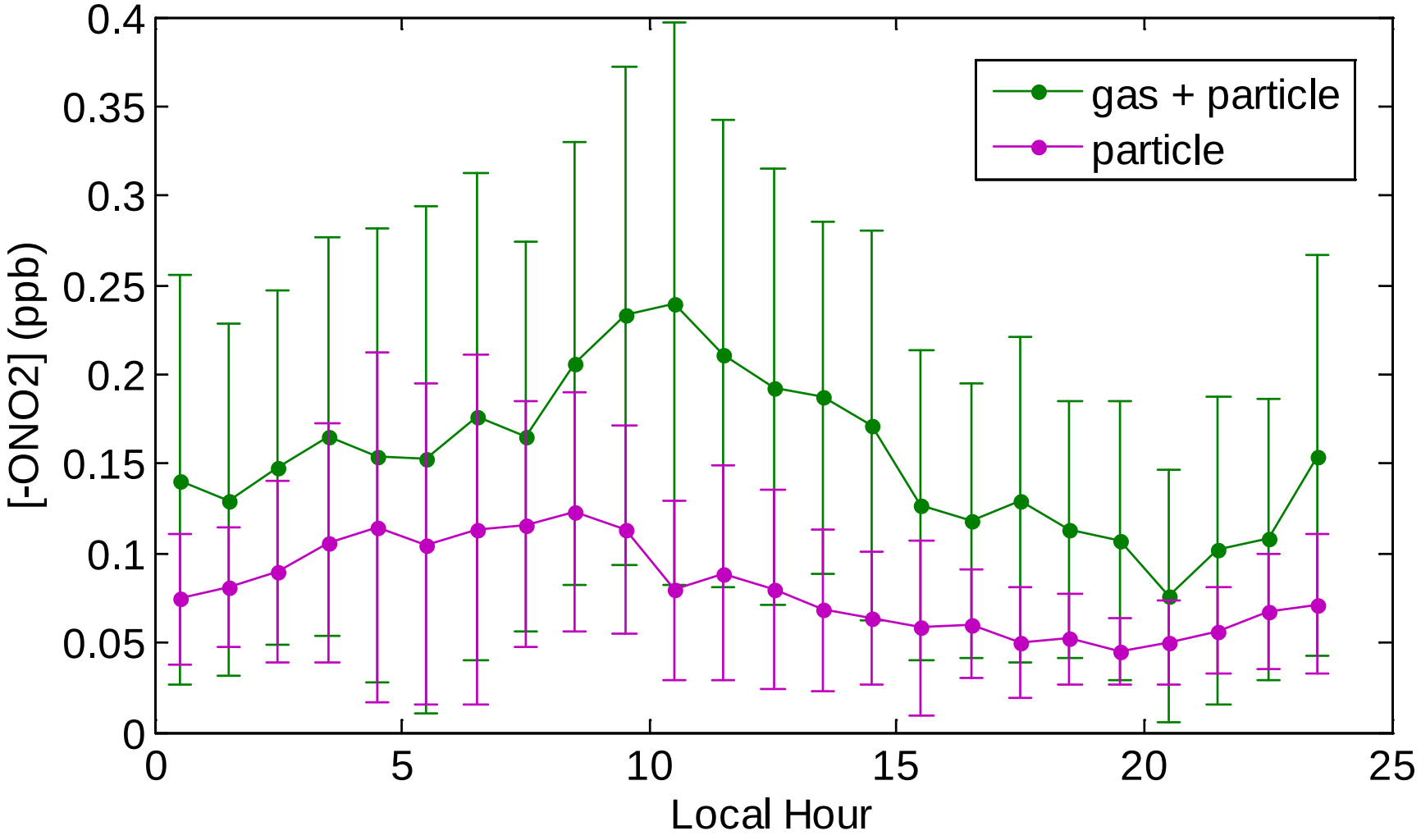
-ONO2 mass only.

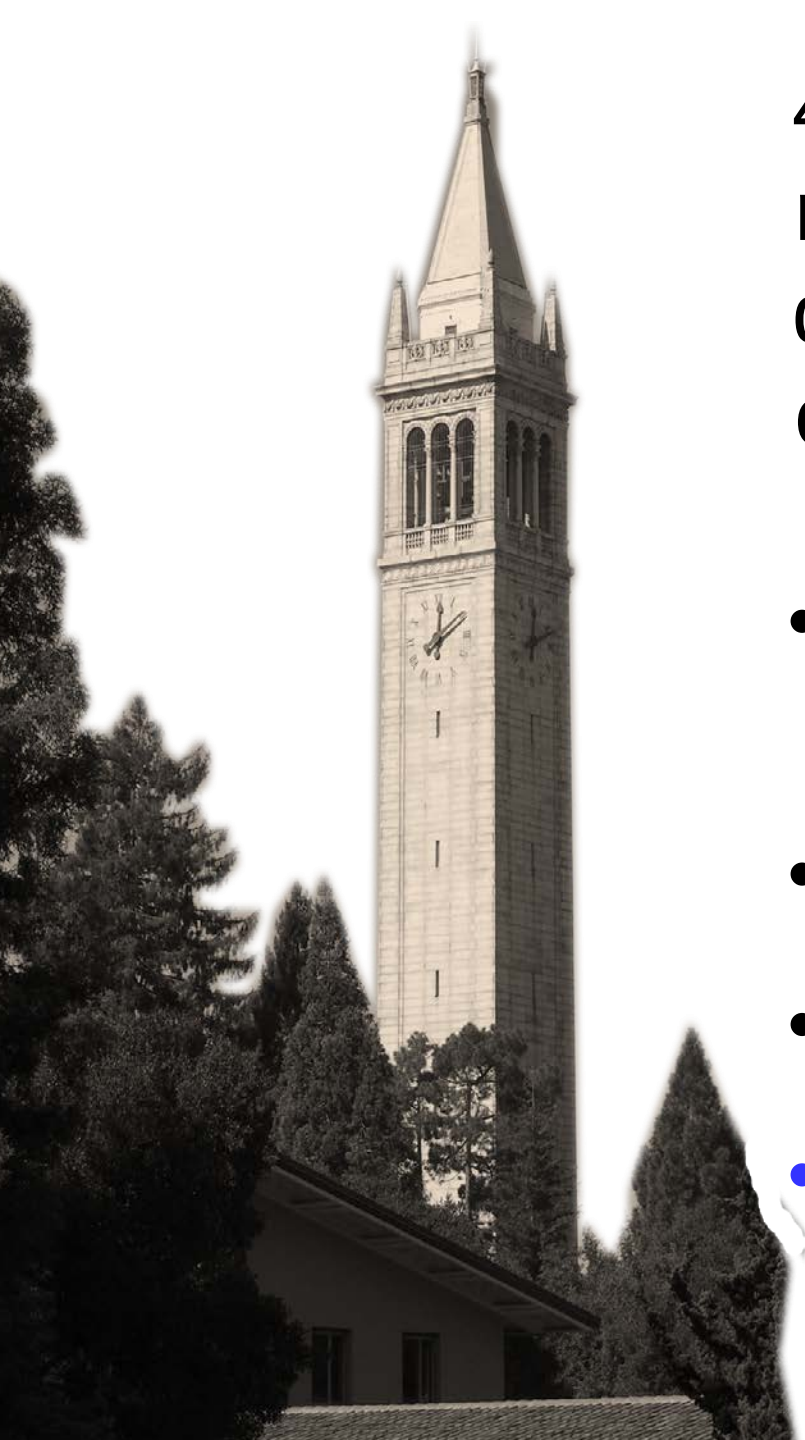
If mass of organic is 200-300 amu, then

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

All of it—NO_3 chemistry??

A first look at NO_x sources and $RONO_2$ Chemistry during SOAS – Rural Alabama June/July 2013





4 strategies toward a mechanistic description of the N-cycle

- Space based trends in emissions
- Eddy fluxes
- Aerosol $RONO_2$
- Fires and soils from space

R.C. Hudman, et al.

Interannual variation in soil NOx emissions observed from Space ACP, 2010.

Steps towards a mechanistic model of global soil nitric oxide emissions: Implementation and space-based constraints, ACP 2012

NITRIC OXiDE: LOW YIELD PRODUCT OF NITRIFYING BACTERIA

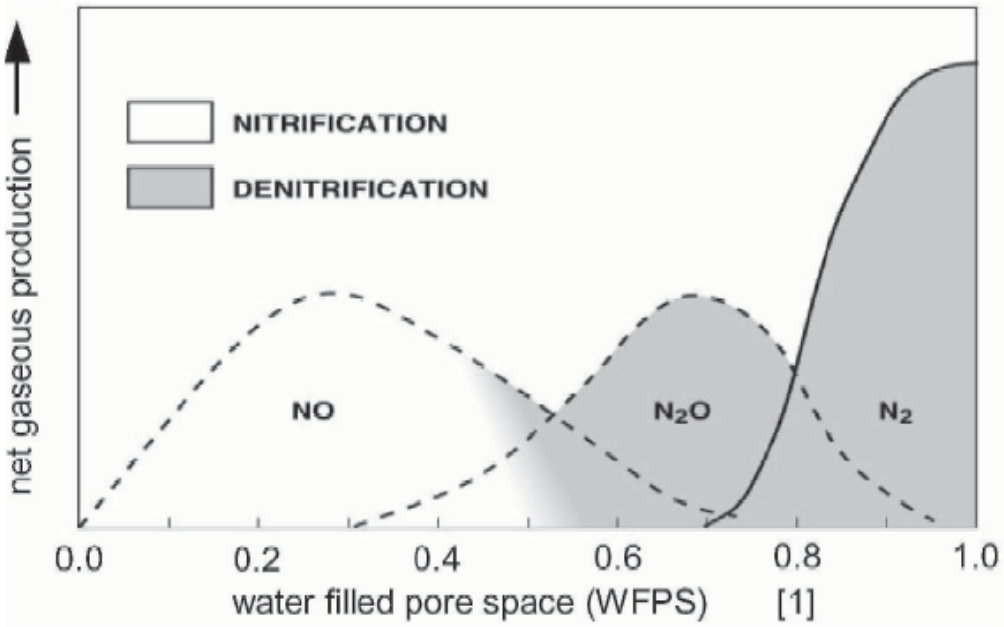
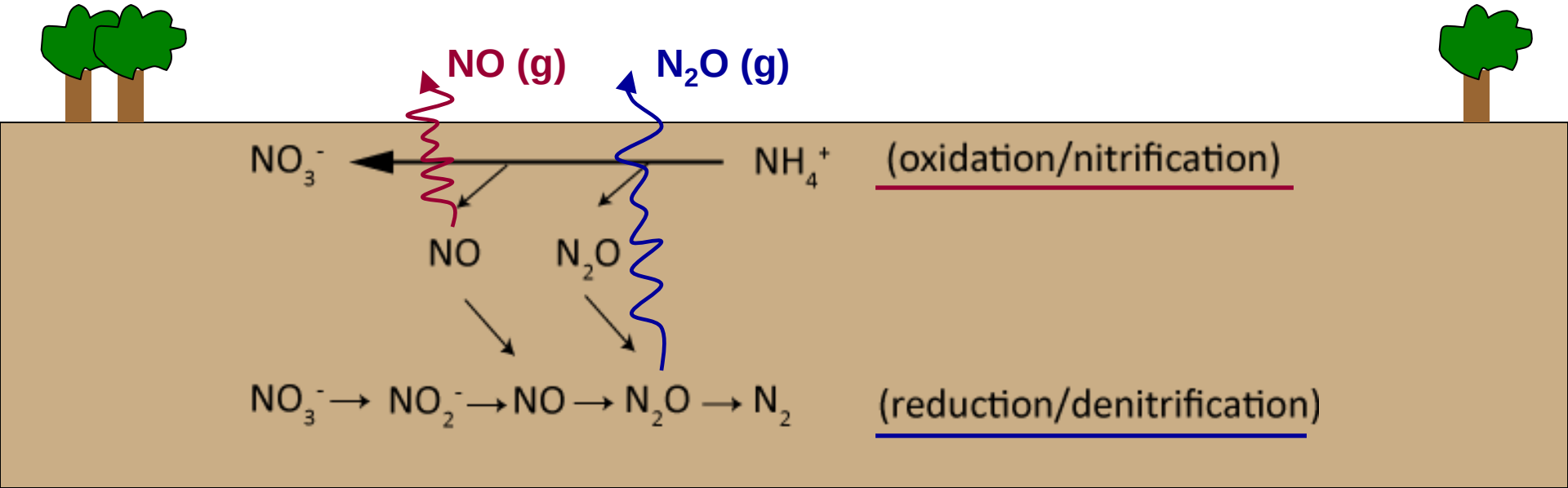
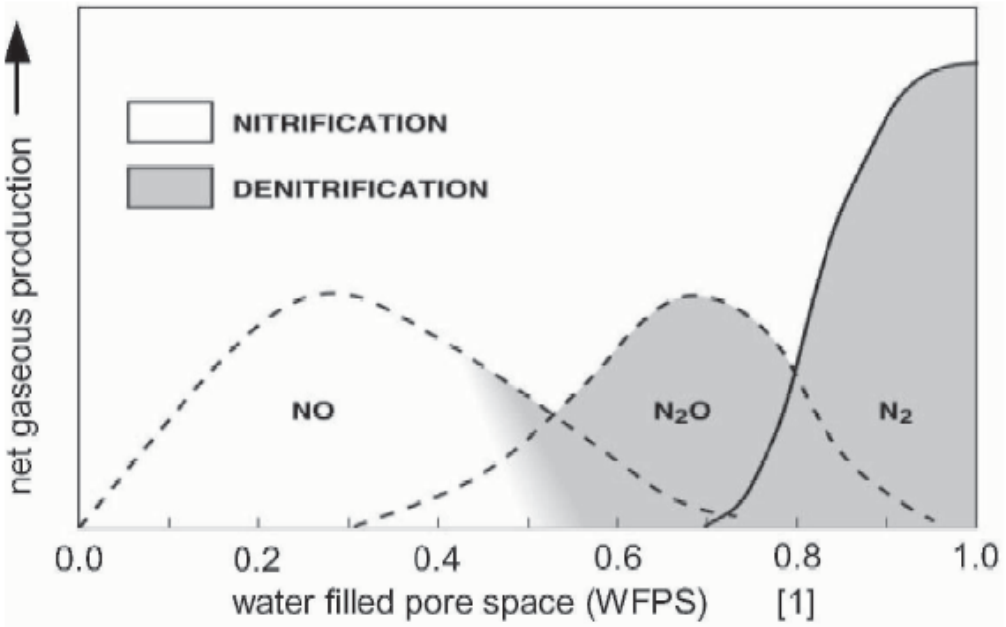


Figure from
Meixner and Yang, Dryland Ecohydrology, 2006



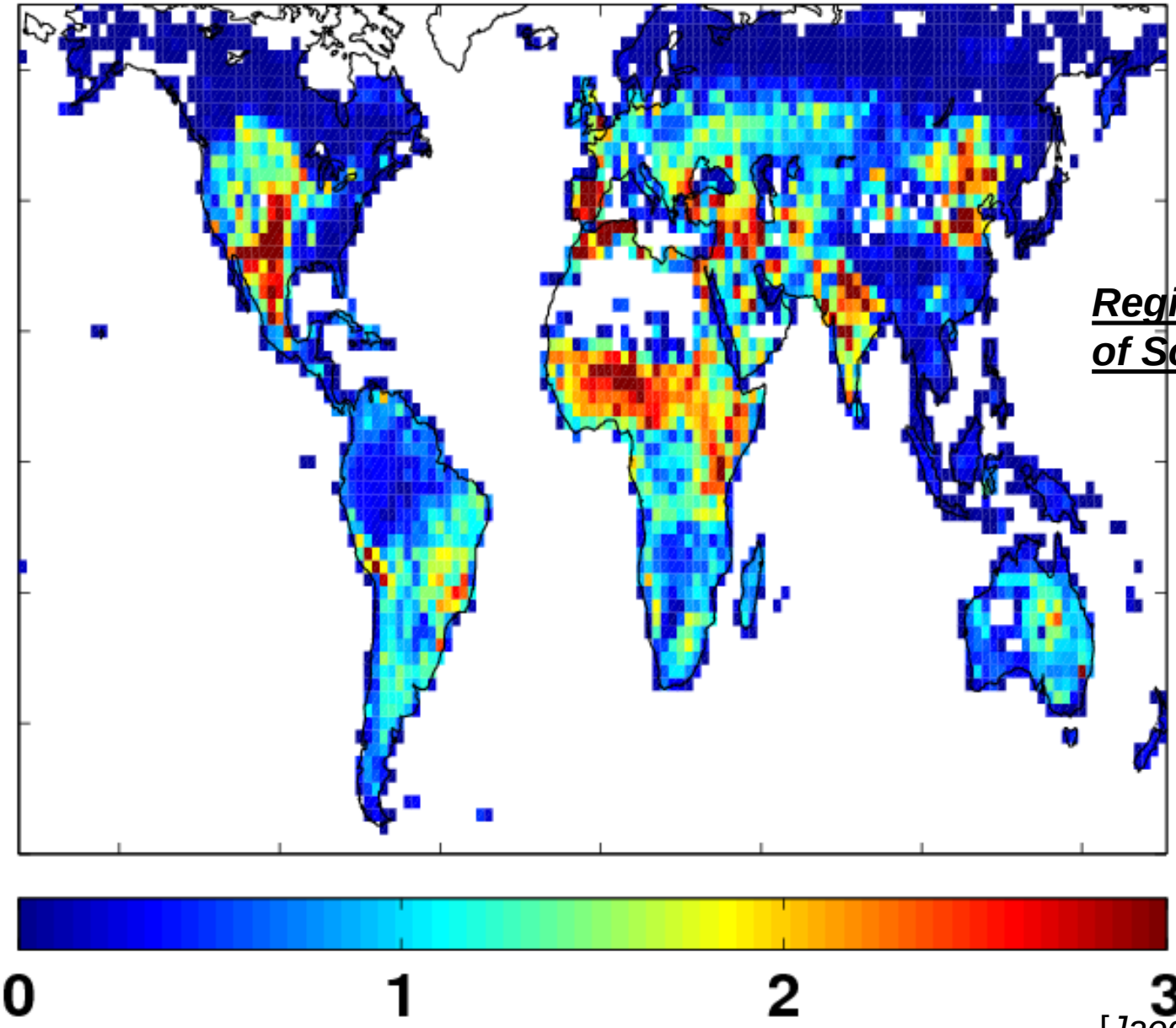
WHERE TO EXPECT LARGE NITRIC OXIDE EMISSIONS:
Fertilized fields and monsoon regions

Pulsing : Release of soil NO following rain event, due N-buildup & reactivation of water-stressed bacteria



- Monsoon:
  1. SW U.S./Mexico
  2. Africa/ITCZ
  3. Southeast Asia
- Fertilized Fields:
  1. United States
  2. Europe

LARGE SOIL NO_x SOURCE INFERRED FROM SATELLITES

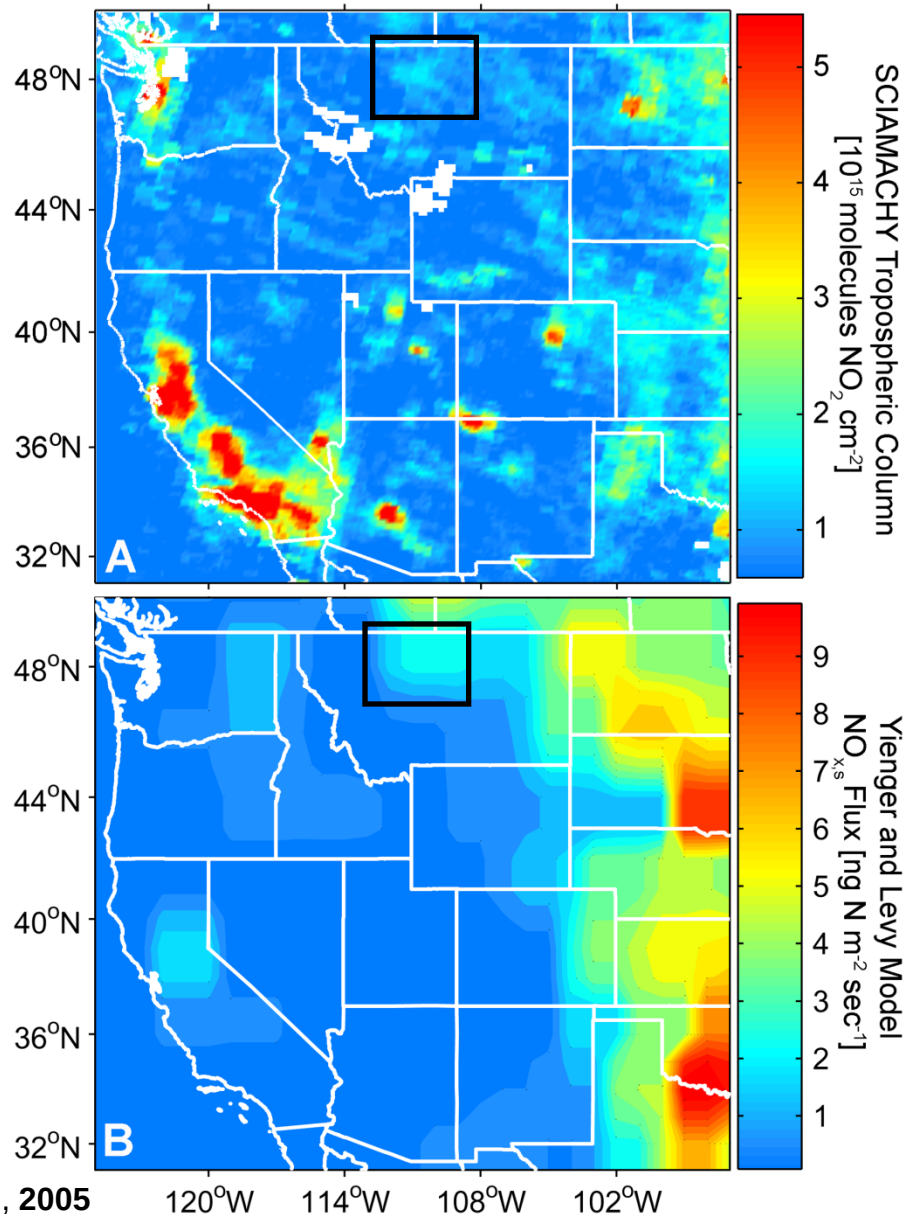


Regional Distribution of Soil Source

8.9 Tg N yr^{-1}

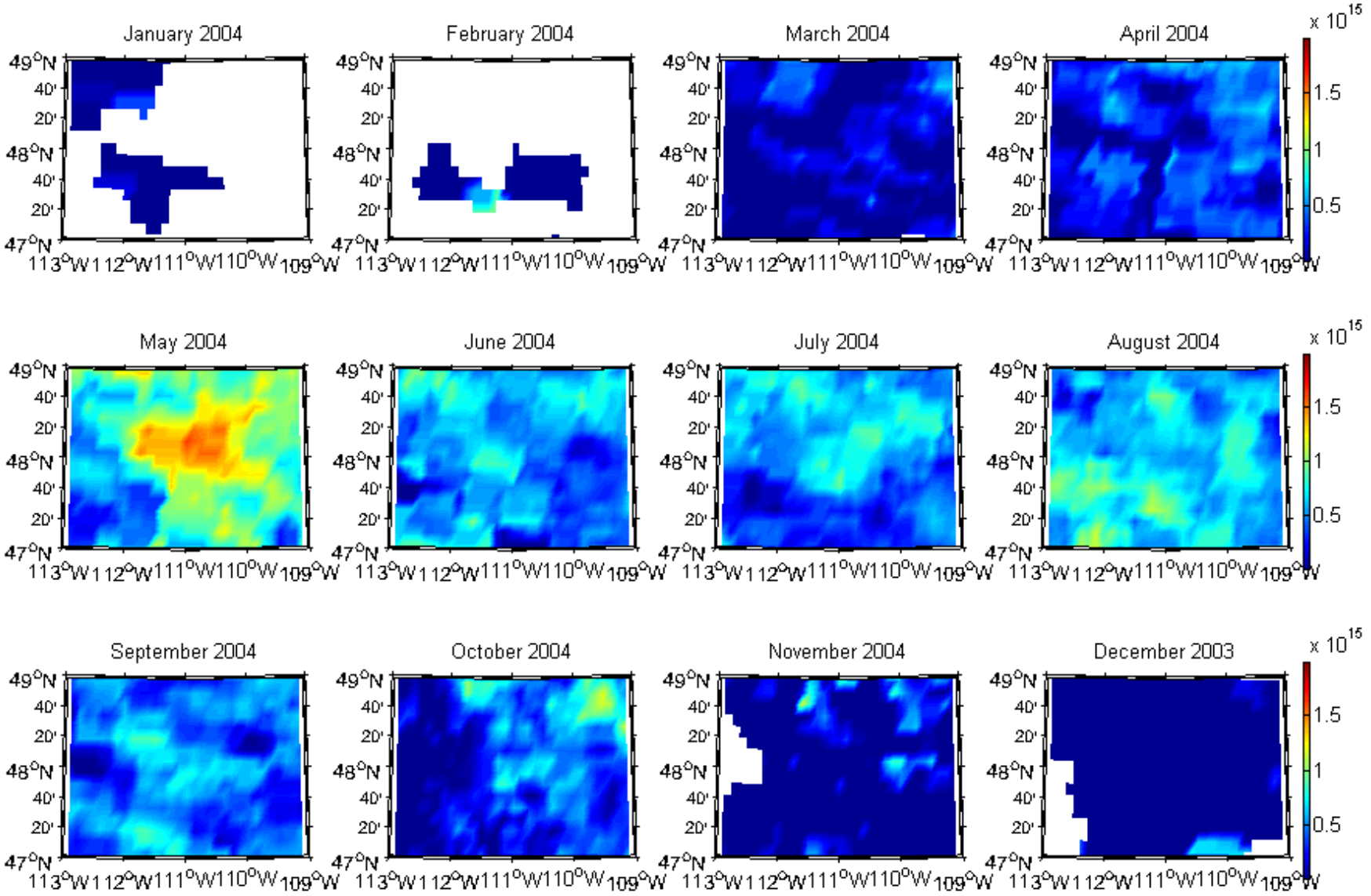
[*Jaeglé et al.*, PNAS, 2005]

Satellite Constraints on Soil NO_x Emissions



Bertram et al., *Geophys. Res. Let.*, **2005**

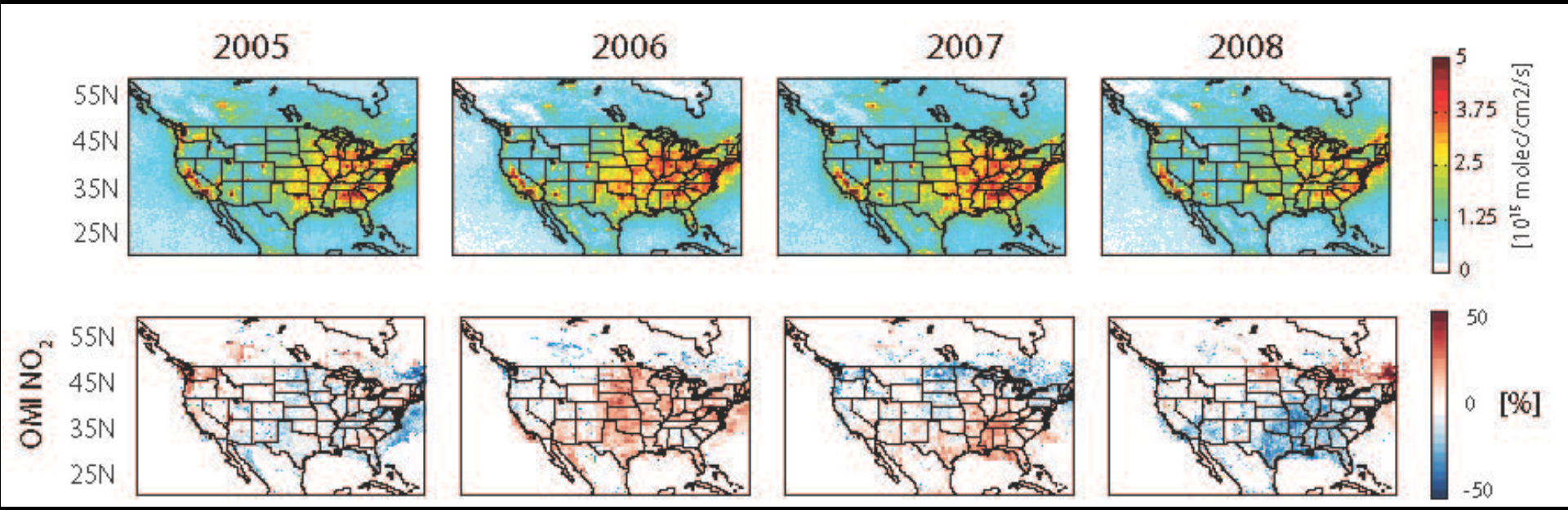
Soil Emissions from fertilized agriculture



Bertram, Heckel, Richter, Burrows and Cohen, GRL 32 L24812 2005

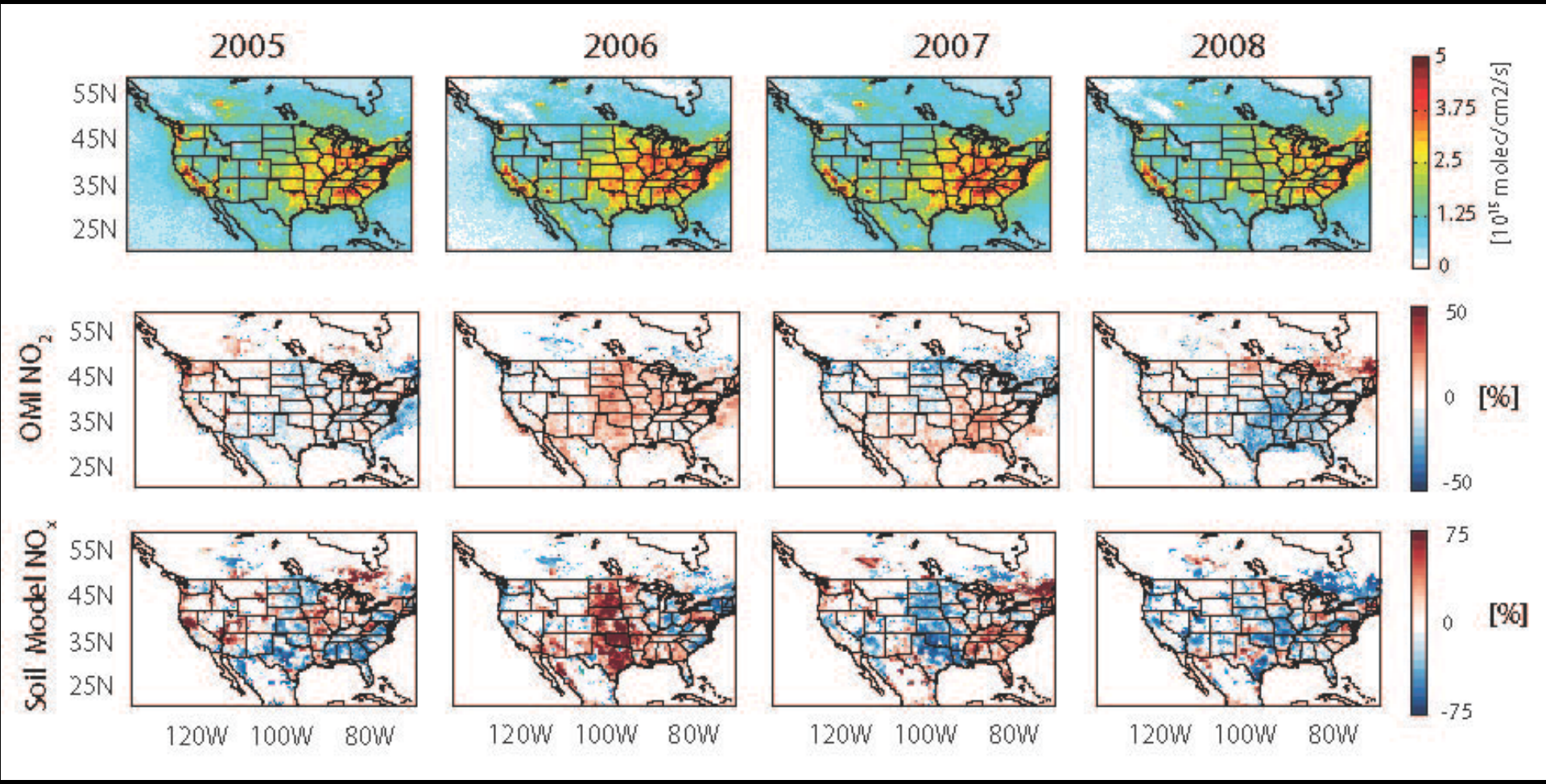
OMI NO_2 ANOMALY

June



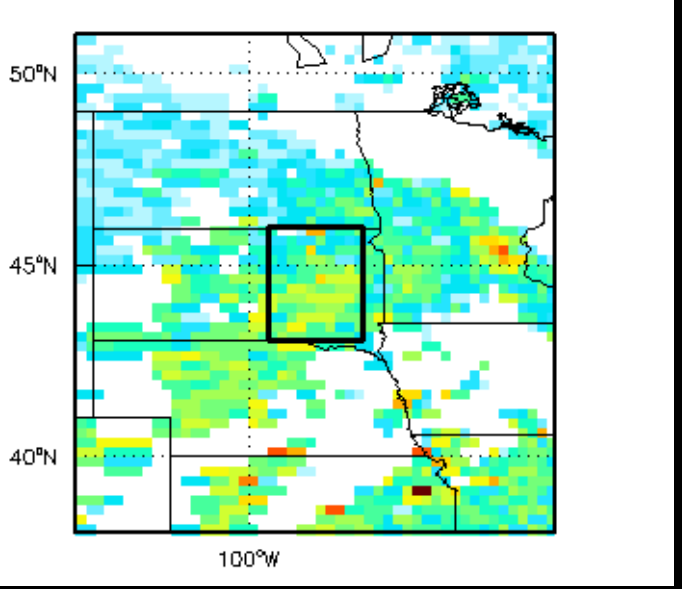
OMI NO_2 ANOMALY

June

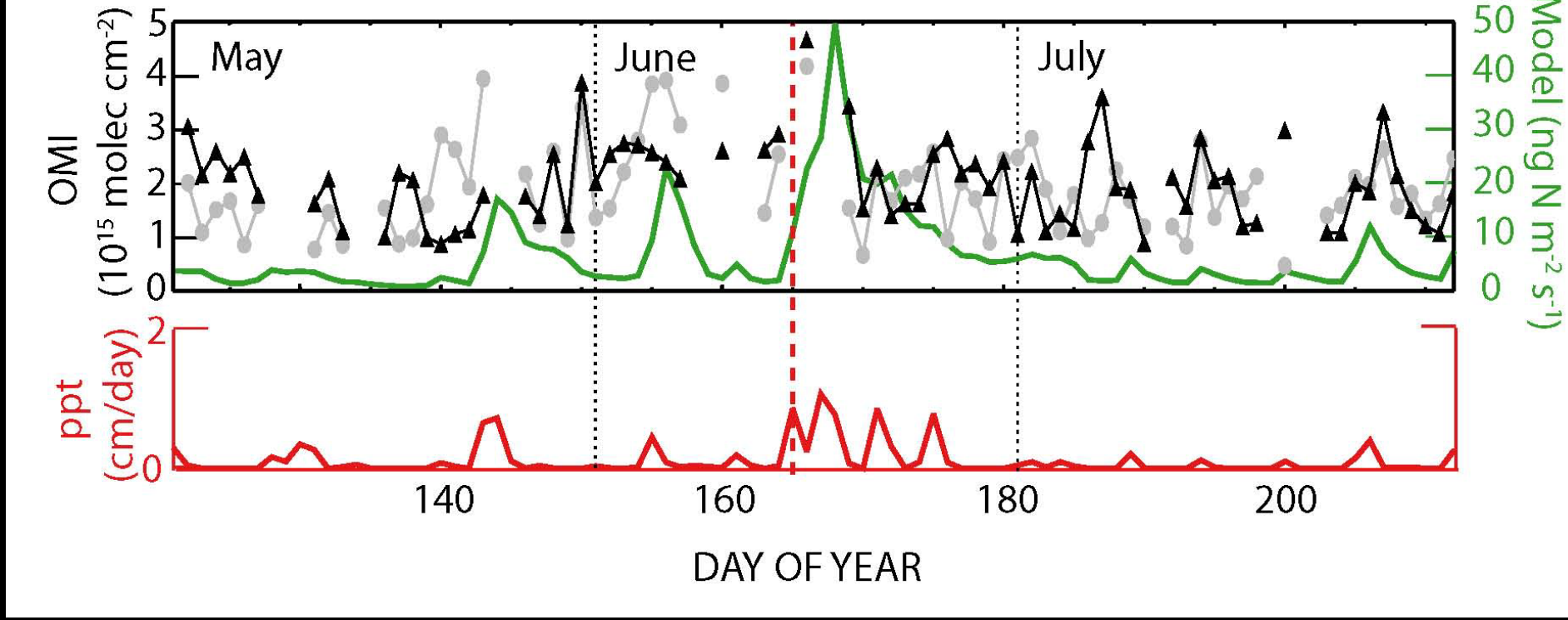


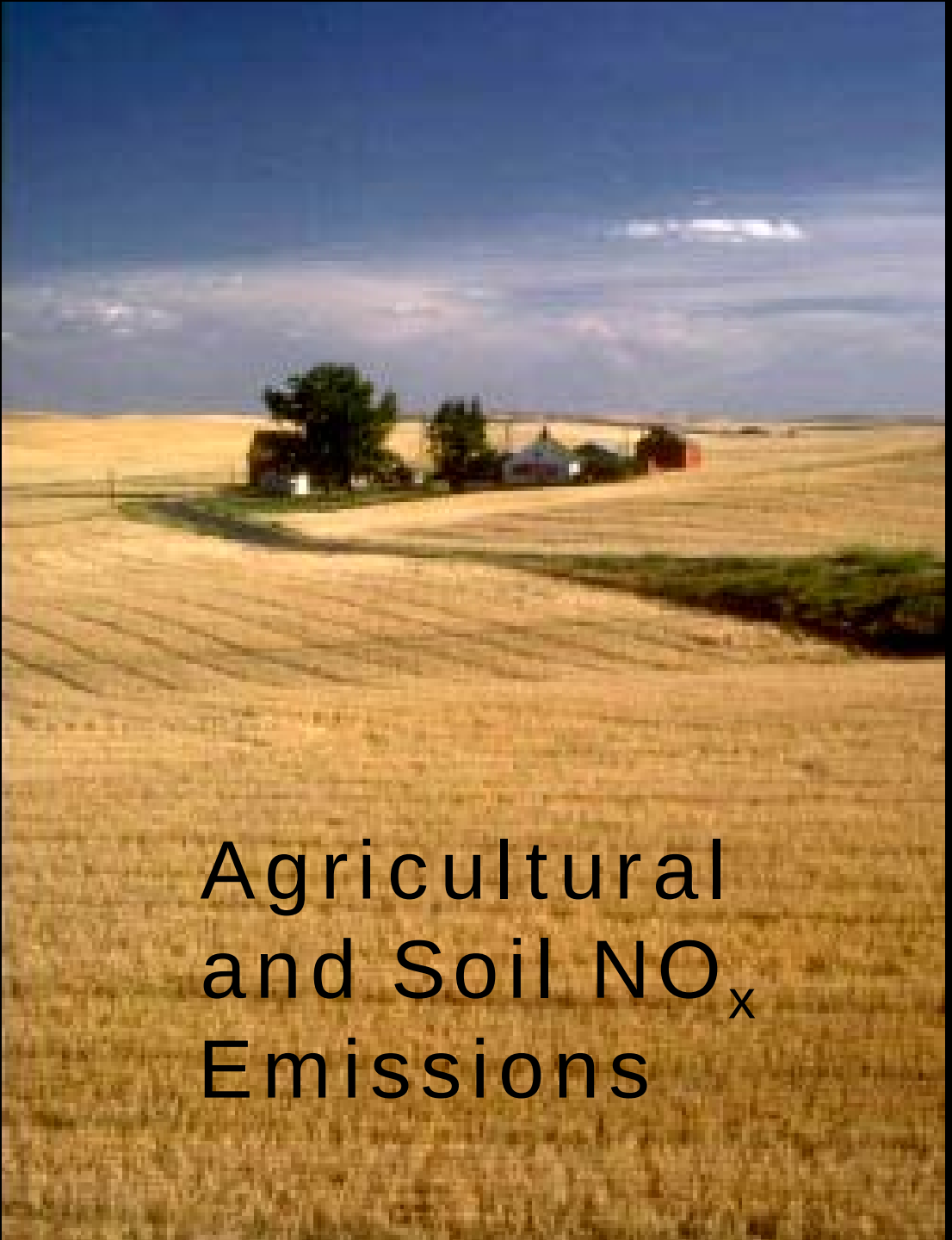
Large scale features match.

What about pulsing?


50°N
45°N
40°N
100°W

Pulsing


OMI
(10^15 molec cm^-2)
May
June
July
Model (ng N m^-2 s^-1)
ppt
(cm/day)
DAY OF YEAR



Agricultural and Soil NO_x Emissions

Large scale behavior consistent with models.

Observed interannual anomaly is similar to model predictions.

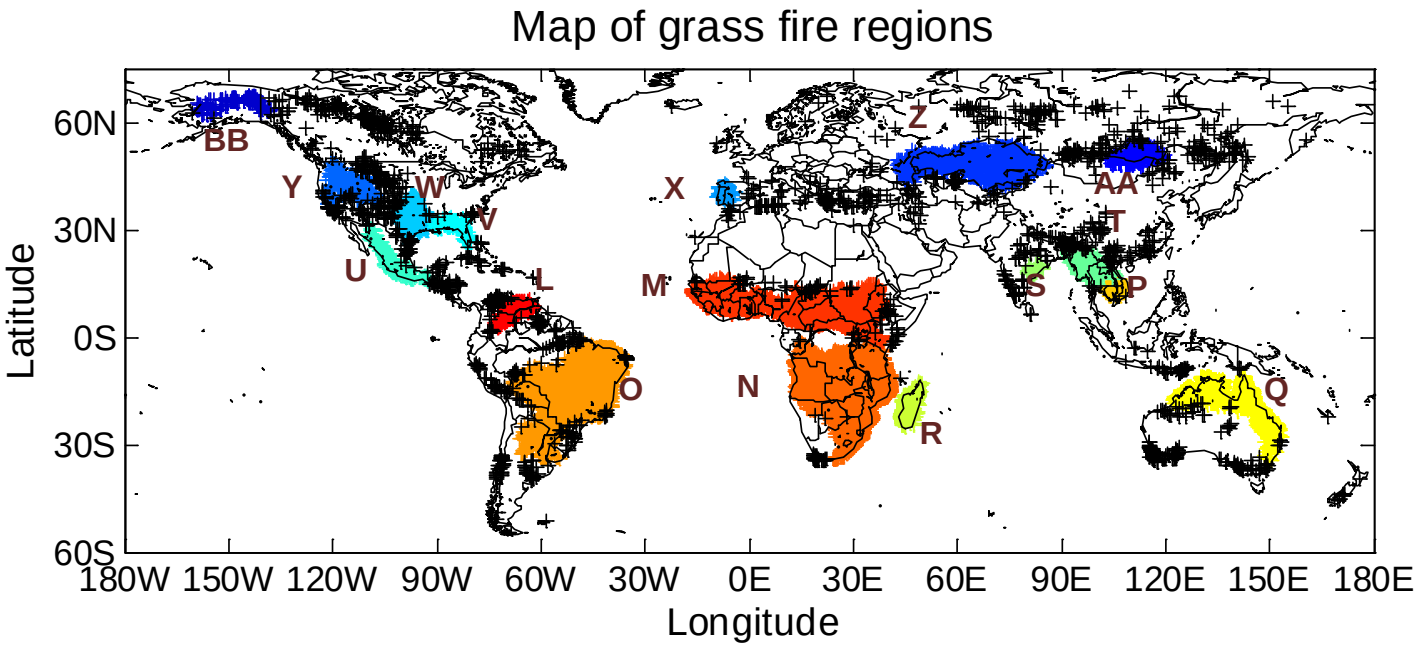
Mechanistic details of pulses bear some resemblance.

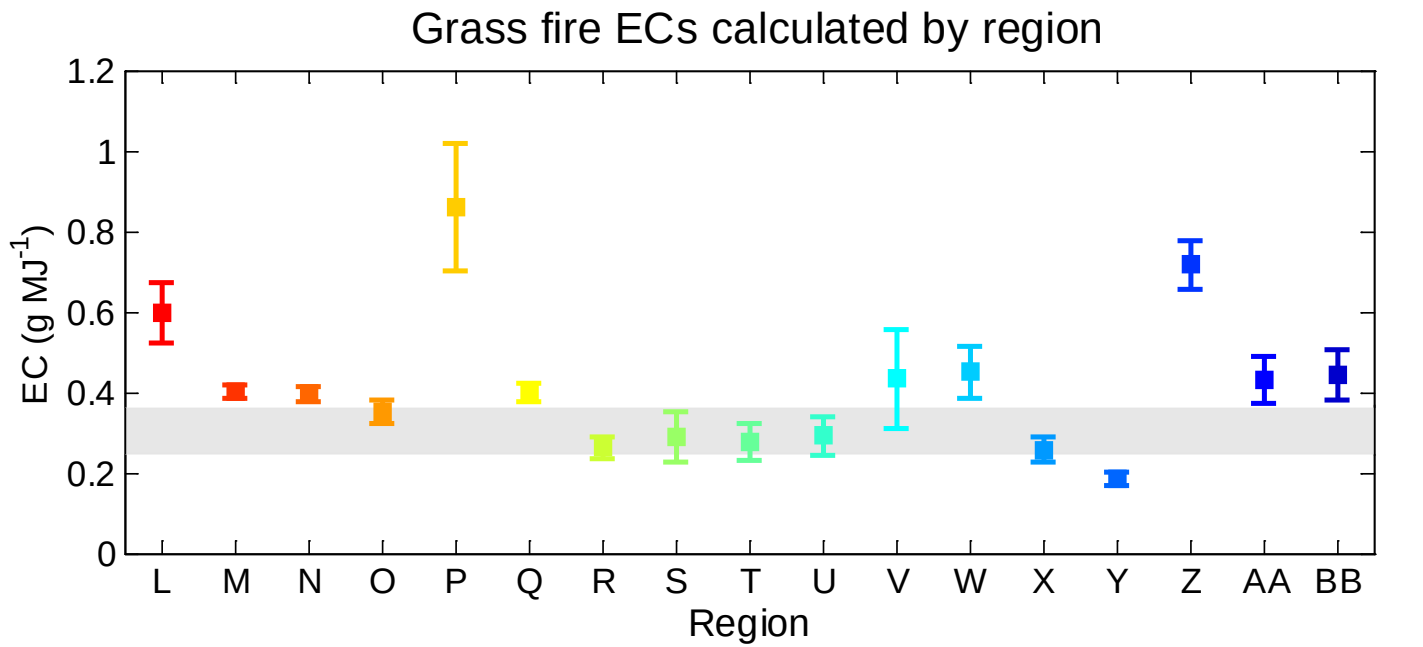
Learning about the process of soil NO_x emissions remains a challenge.

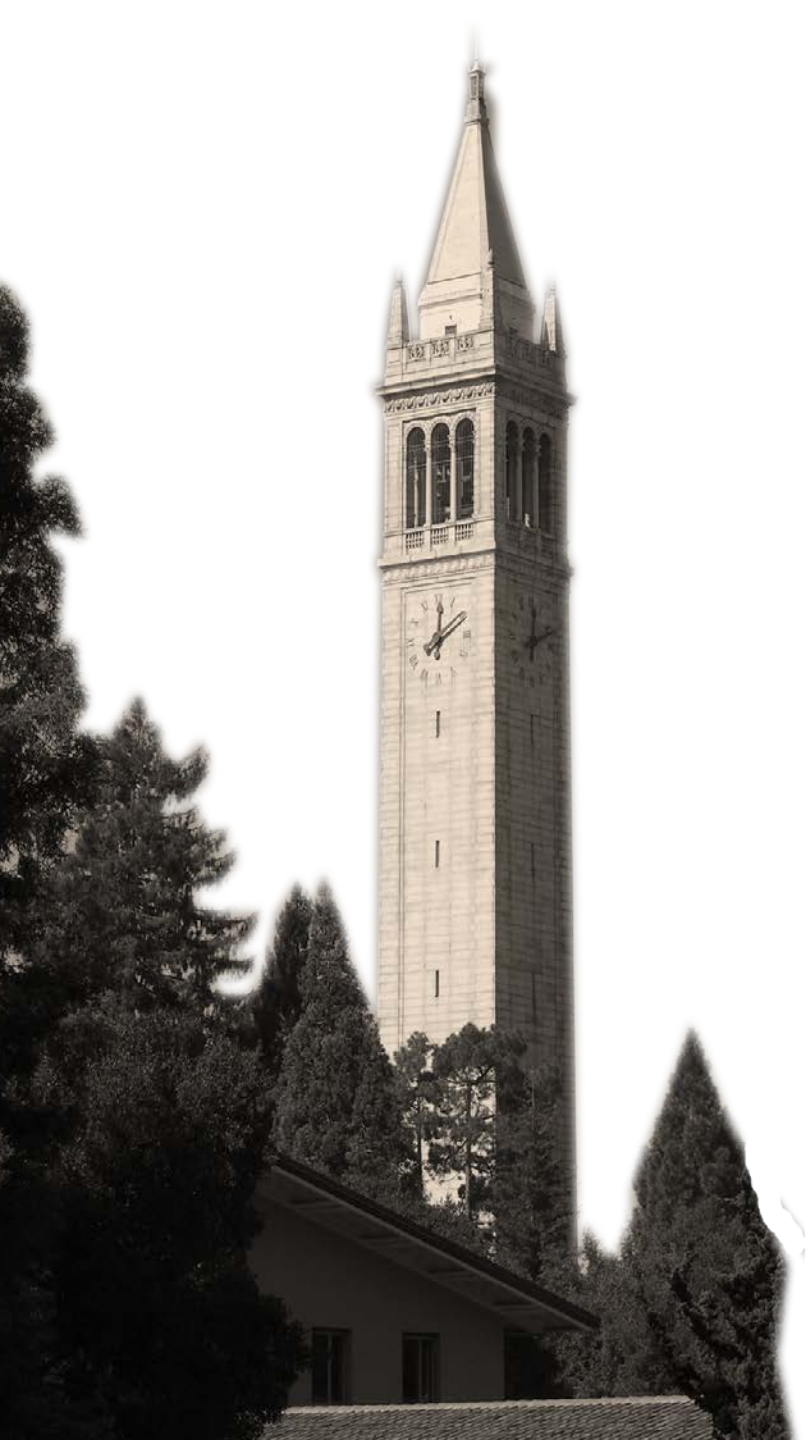
A. Mebust, et al.
ACP 2011

Mebust and Cohen
GRL 2013

Mebust and Cohen,
ACPD 2013

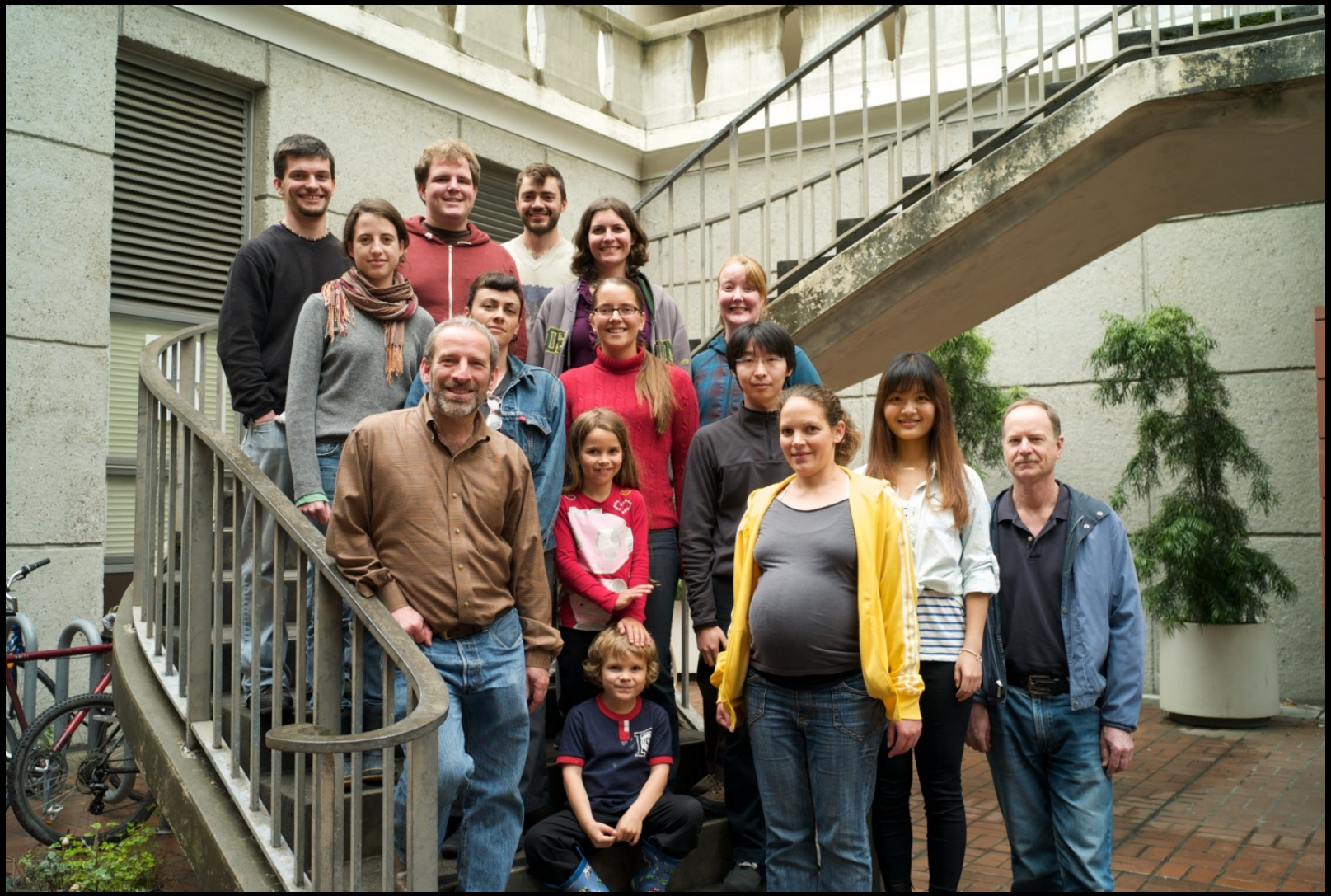

Map of grass fire regions
60N
30N
0S
30S
60S
Latitude
180W 150W 120W 90W 60W 30W 0E 30E 60E 90E 120E 150E 180E
Longitude
BB
Y
W
V
U
L
X
Z
AA
T
M
S
P
O
N
R
Q


Grass fire ECs calculated by region
1.2
1
0.8
0.6
0.4
0.2
0
EC (g MJ-1)
L M N O P Q R S T U V W X Y Z AA BB
Region



Conclusion

The combination of satellite based instruments, new in situ approaches and laboratory measurements are bringing exciting changes to how we approach describing mechanisms of N exchange and then test our understanding.



Thank you!