NO_x Chemistry during WINTER

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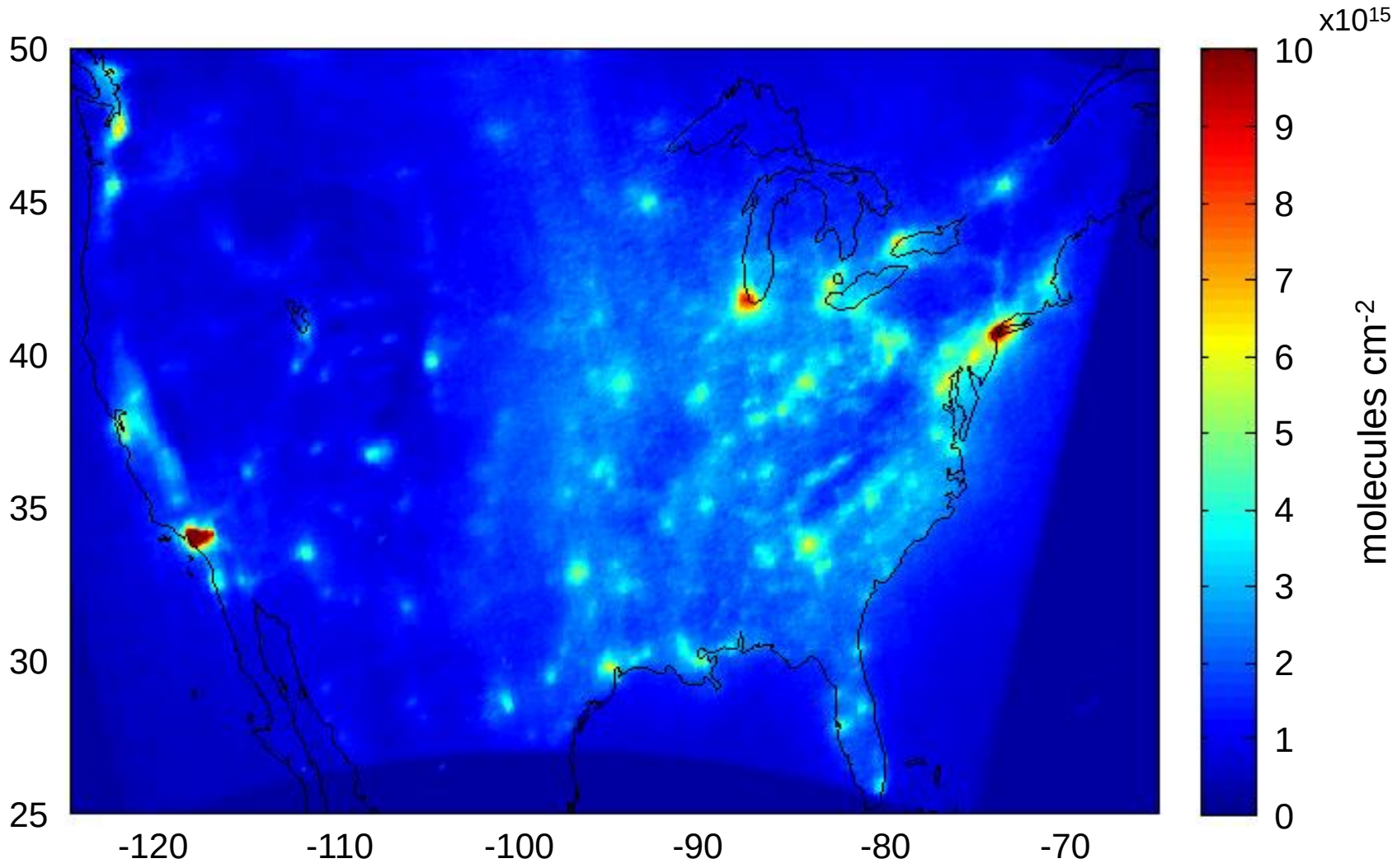
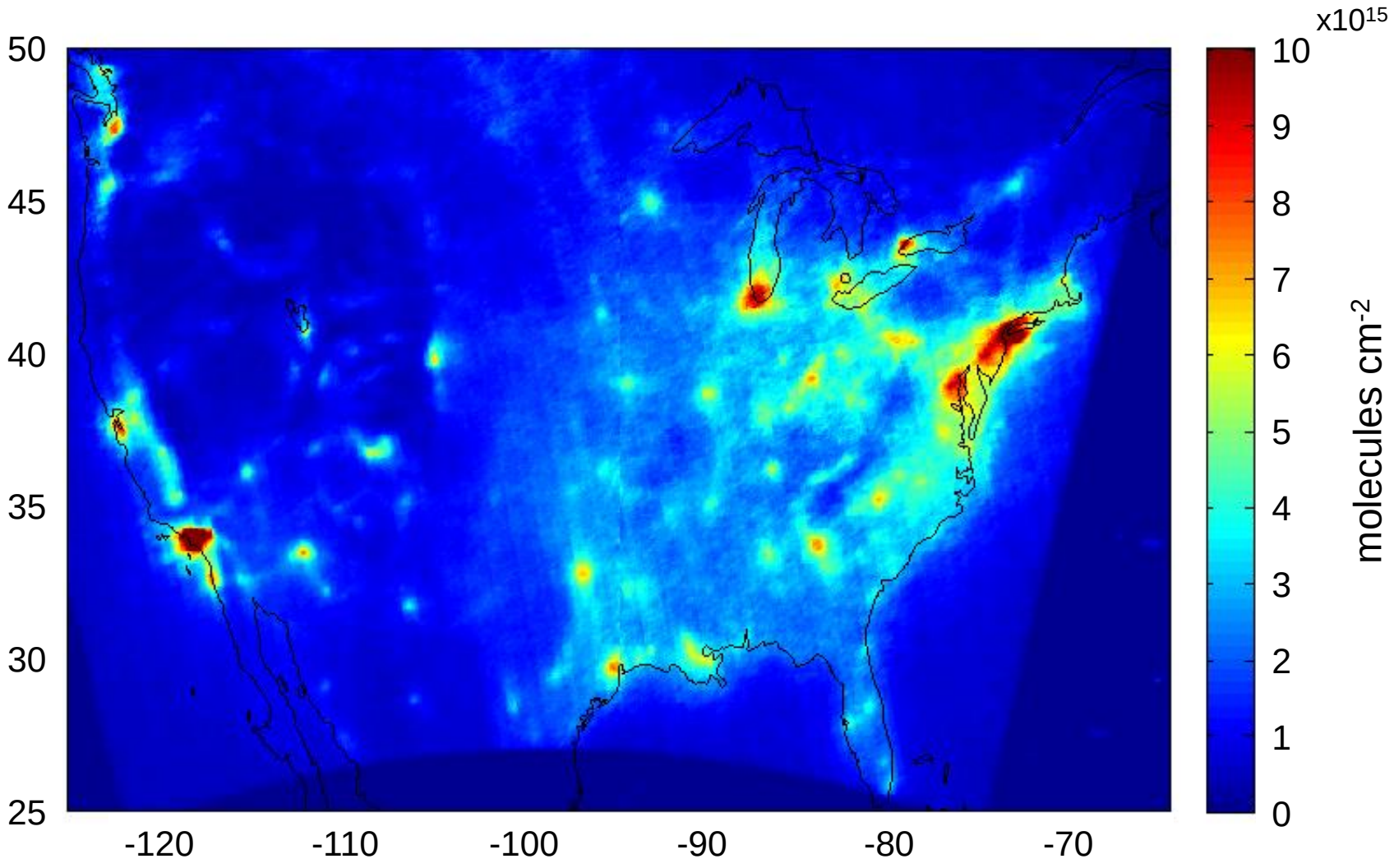
Summer-average NO_2 columns in 2011

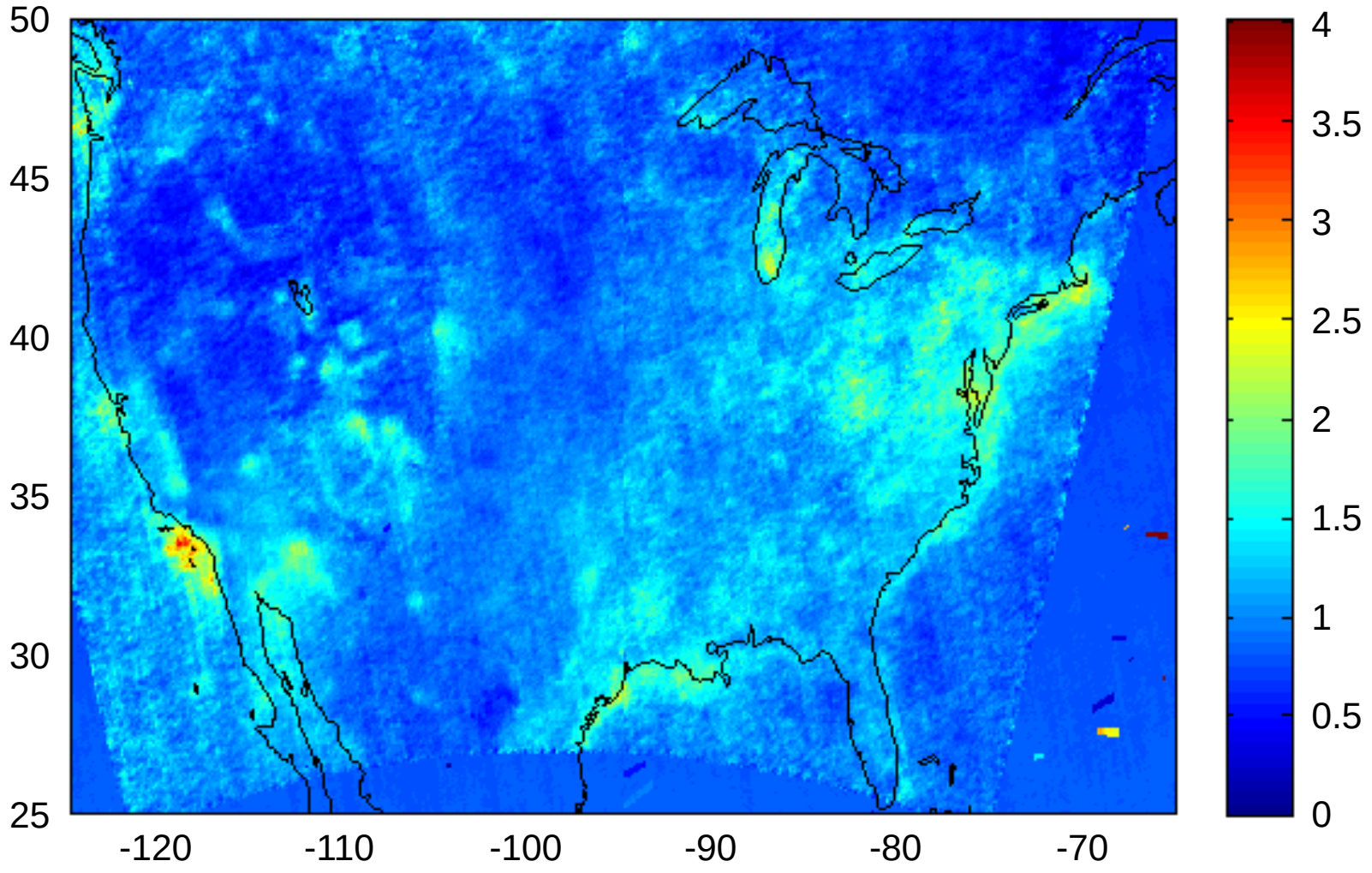


Russell, A. R.; Perring, A. E.; Valin, L. C.; Bucsela, E. J.; Browne, E. C.; Wooldridge, P. J.; Cohen, R. C. *Atmos. Chem. Phys.* **2011**, *11*, 8543.

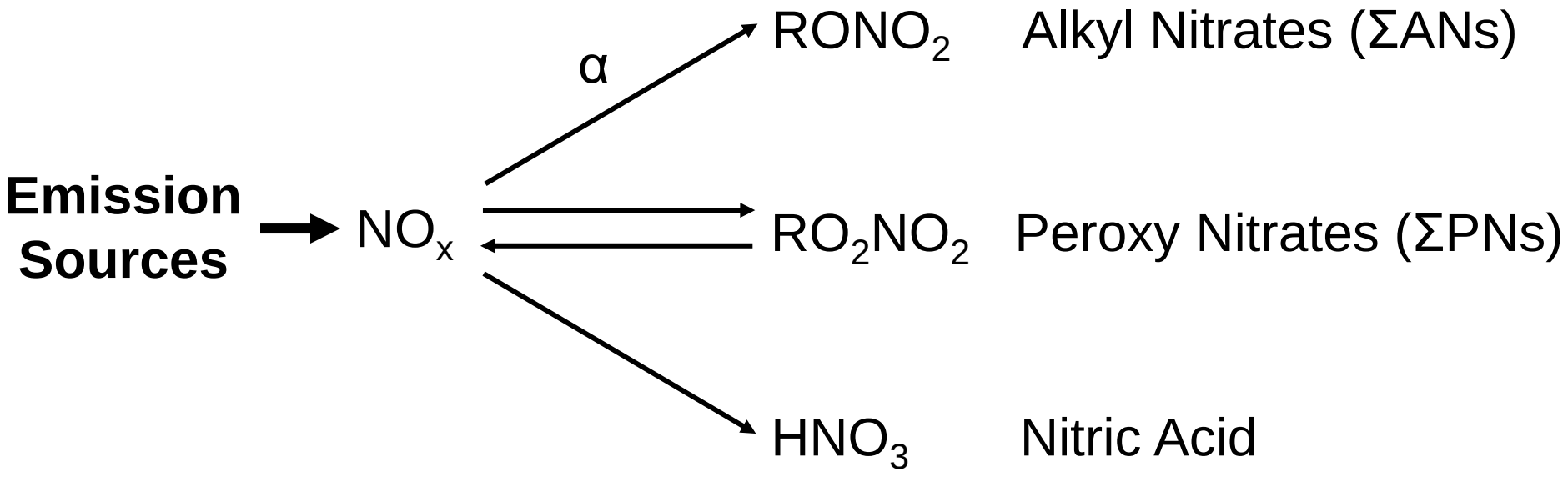
Winter-average NO_2 columns in 2011



The ratio of winter to summer NO_2 columns in 2011

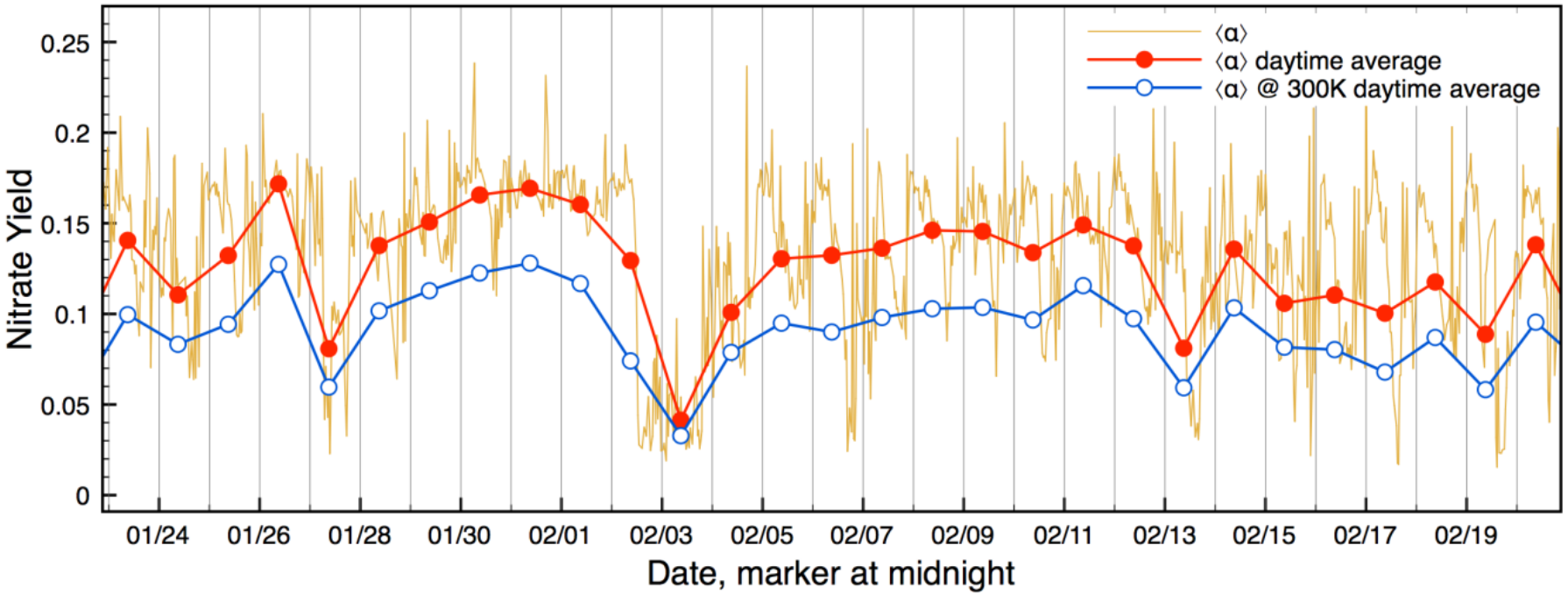


NO_x lifetime is controlled by its sinks



$NO_x \equiv NO + NO_2$

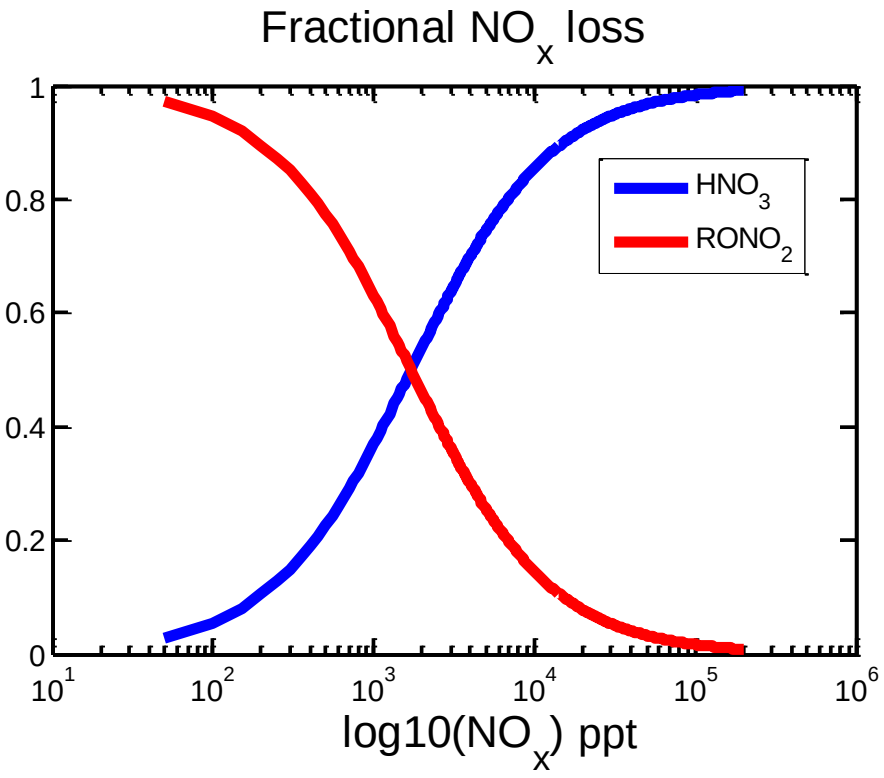
Temperature dependence of alkyl nitrate formation branching ratio (α)



Uintah Basin, Winter 2012

Lee, L.; Wooldridge, P. J.; Gilman, J. B.; Warneke, C.; de Gouw, J.; Cohen, R. C. *Atmos. Chem. Phys. Discuss.* **2014**, *14*, 17401.

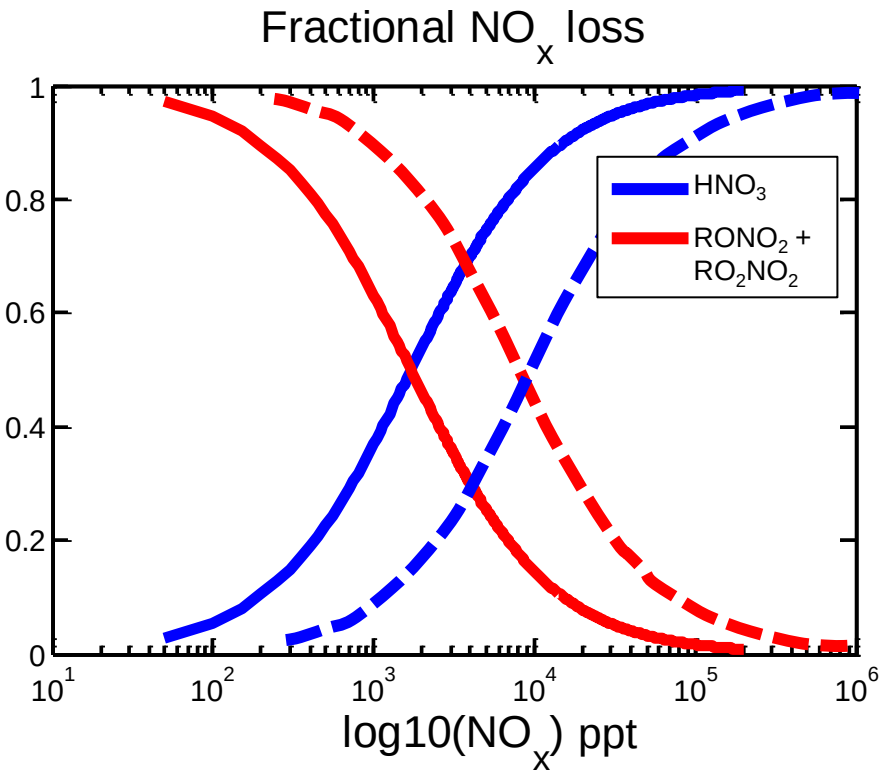
Sinks of NO_x



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

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

Sinks of NO_x

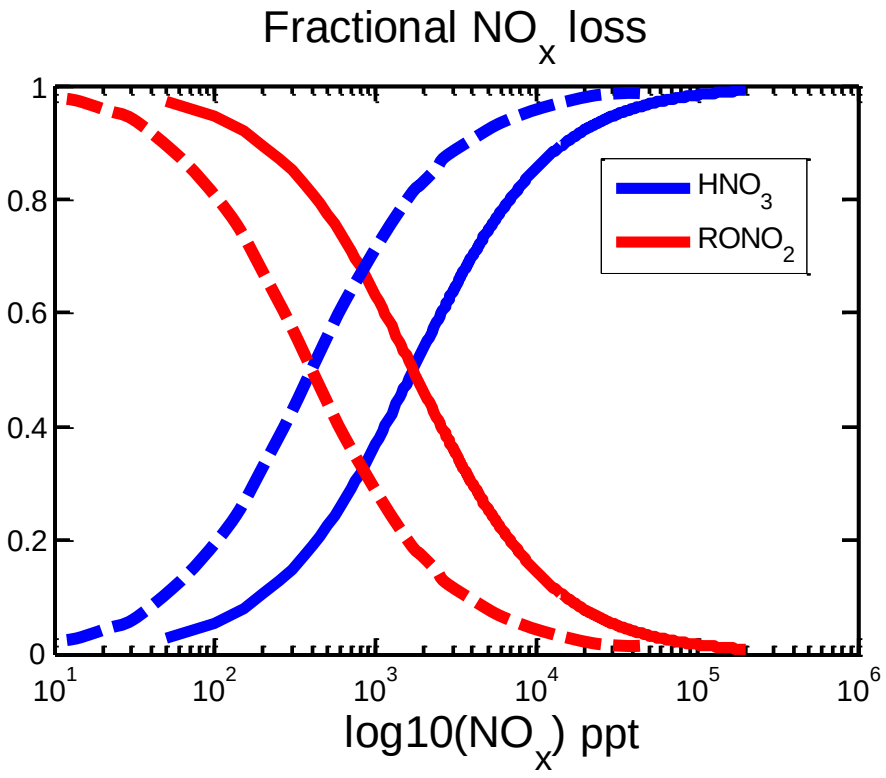


$$NO_2 + OH \xrightarrow{M} HNO_3$$

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

In winter, peroxy nitrate lifetimes are longer.

Sinks of NO_x



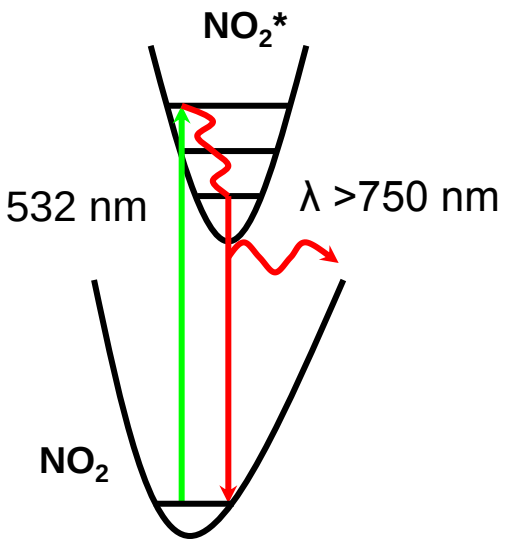
$$NO_2 + OH \xrightarrow{M} HNO_3$$

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

At night:

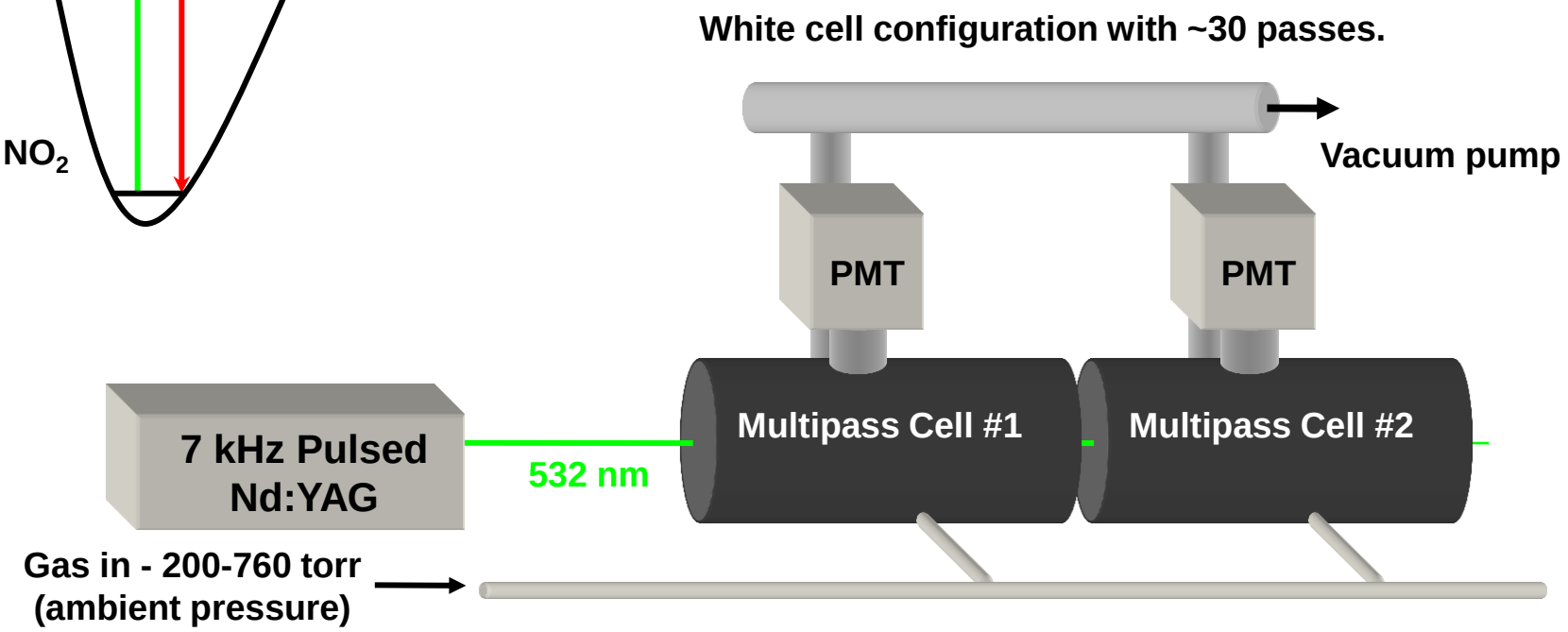
$$N_2O_5 + H_2O \xrightarrow{M} HNO_3$$

Laser-induced fluorescence (LIF) detection of NO_2



The limit of detection of the instrument is 25 pptv/10 s for NO_2 at *S/N*=2.

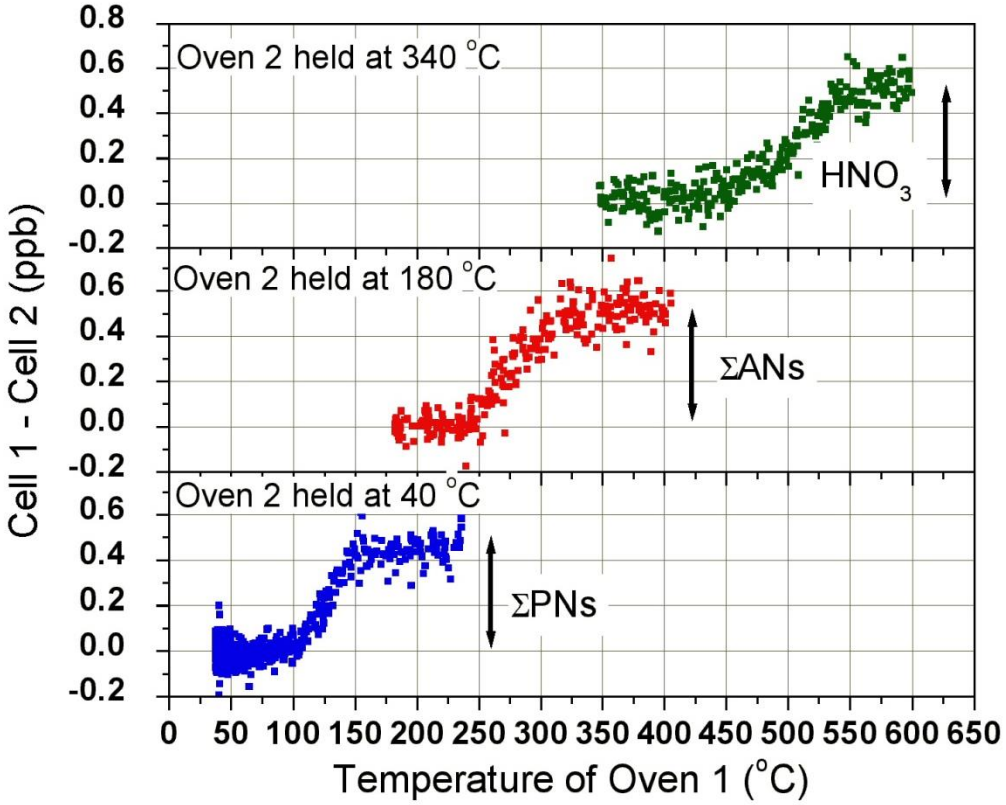
- Calibration done using NO_2 standard
- Zero air used to obtain instrument zero



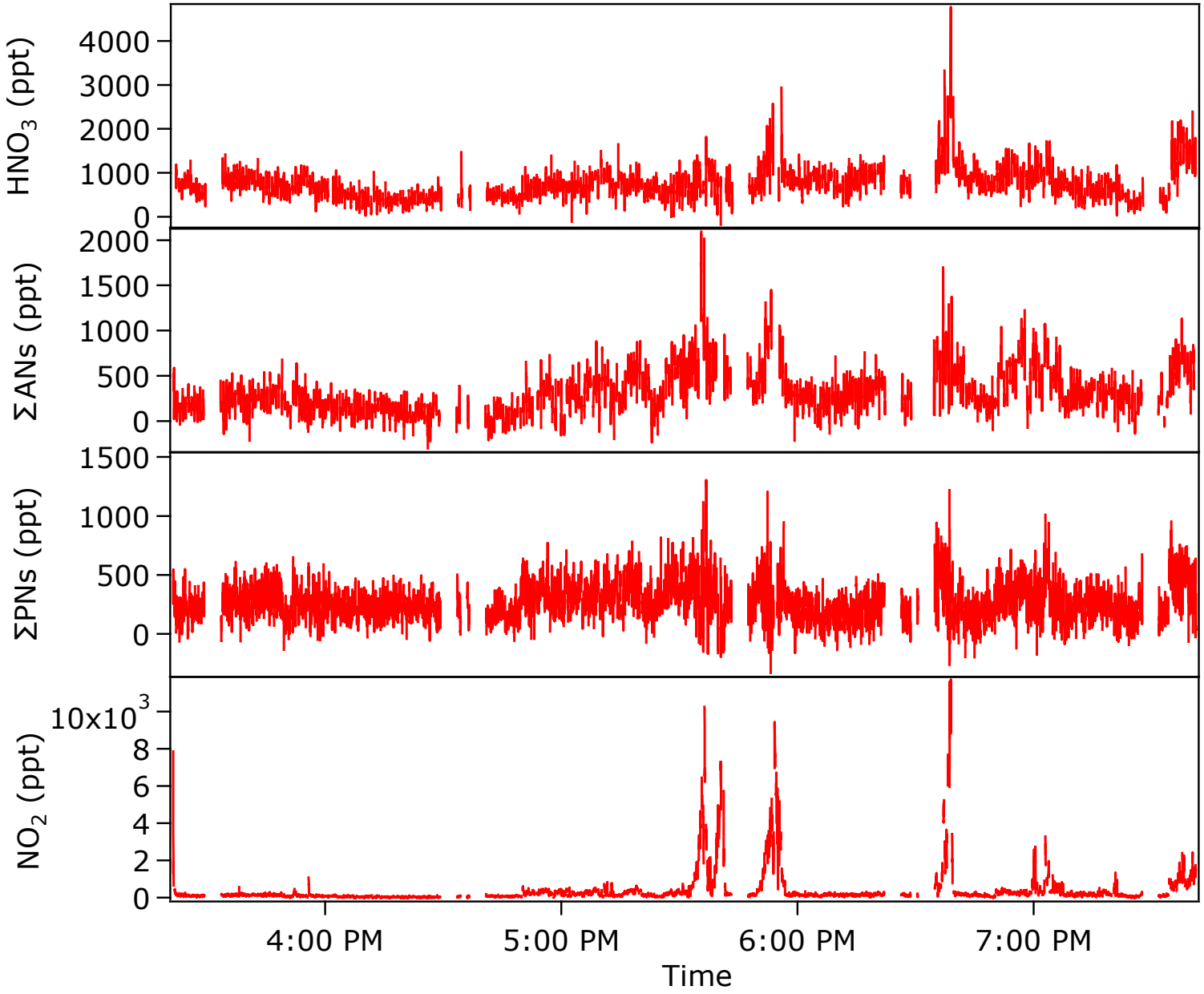
Thornton, J. A.; Wooldridge, P. J.; Cohen, R. C. *Anal. Chem.* **2000**, *72*, 528.
Bertram, T. H.; Perring, A. E.; Wooldridge, P. J.; Dibb, J.; Avery, M. A.; Cohen, R. C. *Atmos. Chem. Phys.* **2013**, *13*, 4617.

Thermal dissociation laser-induced fluorescence (TD-LIF)

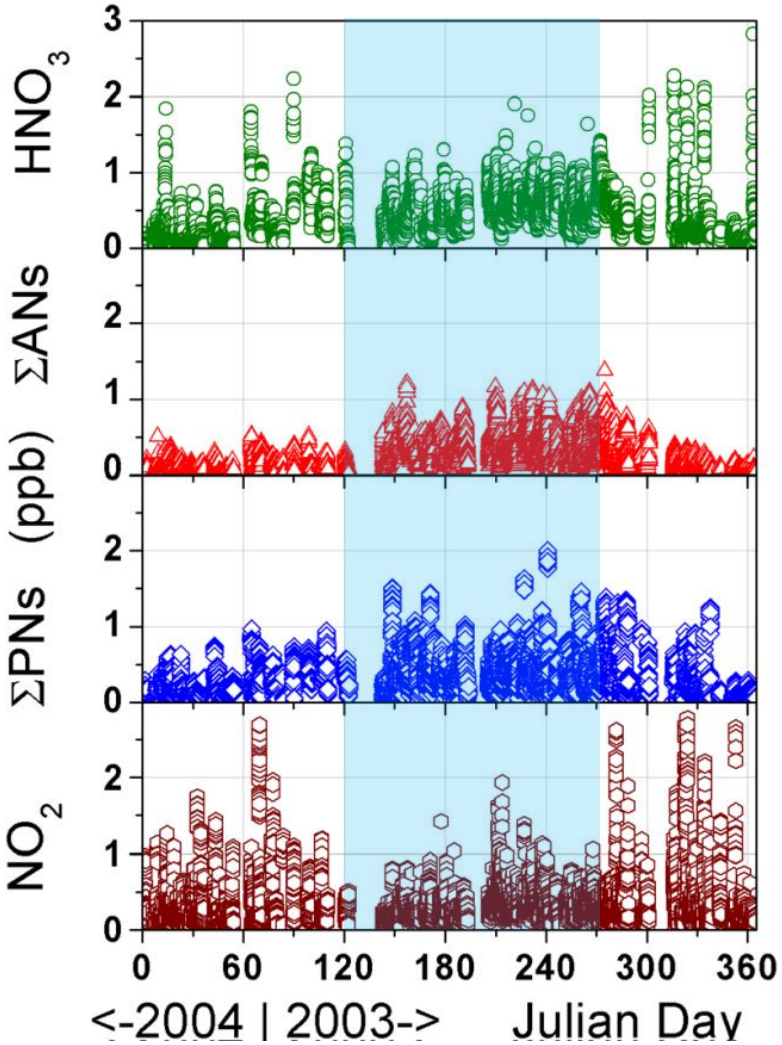
- XNO_2 + heat → NO_2 + X
- Differing bond strengths lead to dissociation at characteristic temperatures.
- Peroxy nitrates (RO_2NO_2) and N_2O_5 dissociate at ~180°C.
- Alkyl nitrates ($RONO_2$) and $ClNO_2$ dissociate at ~340°C.
- Nitric acid (HNO_3) dissociates at ~600°C.



TD-LIF data


HNO3 (ppt)
4000
3000
2000
1000
0
ΣANs (ppt)
2000
1500
1000
500
0
ΣPNs (ppt)
1500
1000
500
0
NO2 (ppt)
10x10^3
8
6
4
2
0
4:00 PM
5:00 PM
6:00 PM
7:00 PM
Time

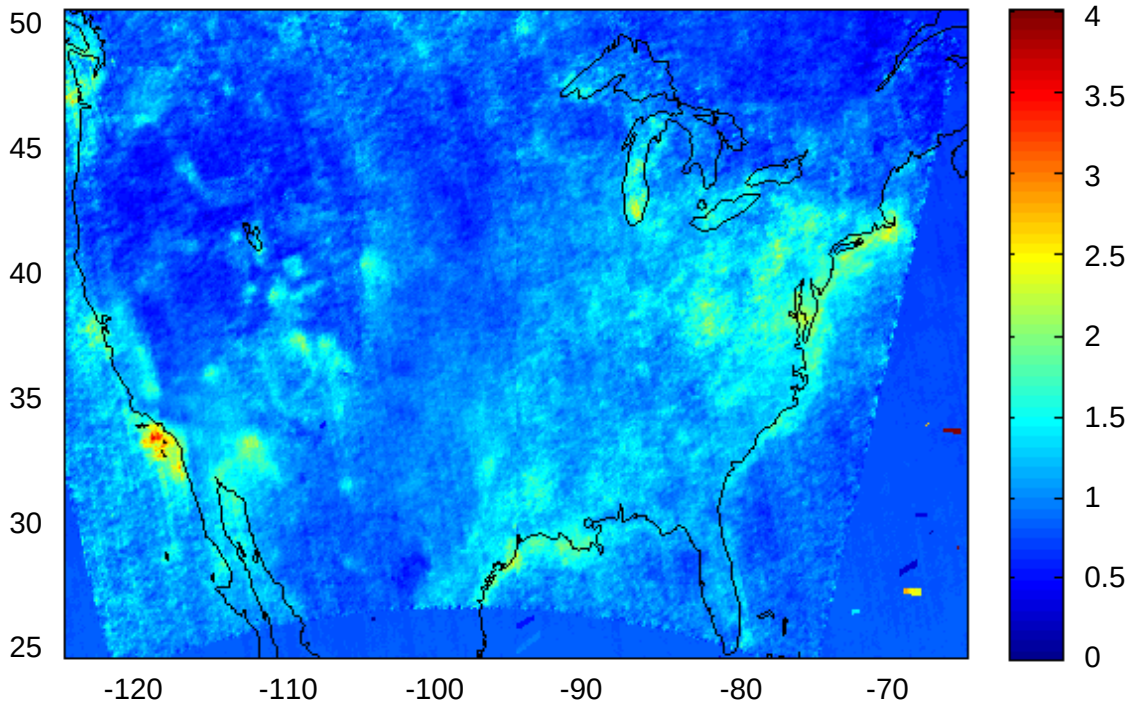
Seasonable variability of N chemistry



Sierra Nevada Mountains, 2003-2004

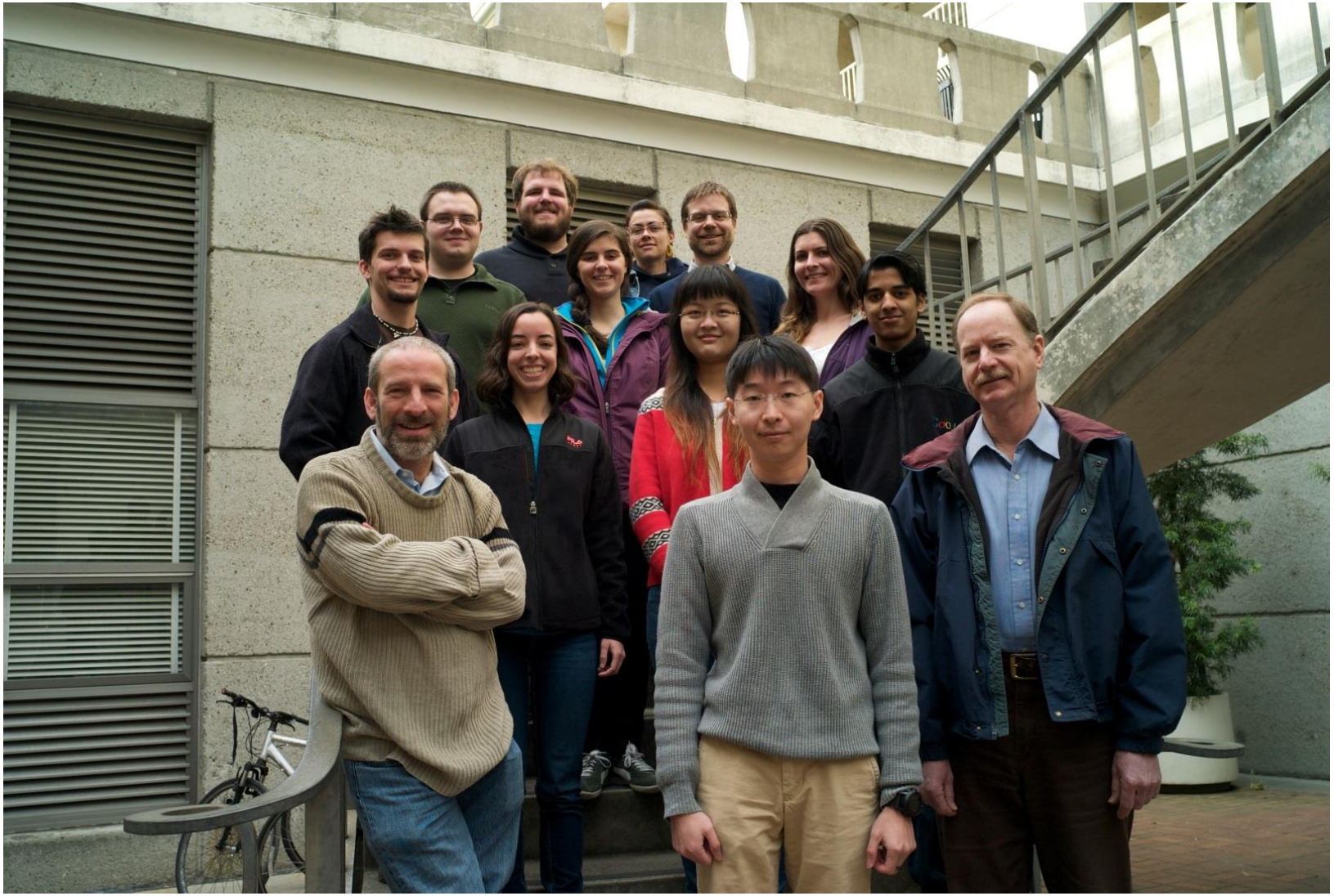
Murphy, J. G.; Day, A.; Cleary, P. A.; Wooldridge, P. J.; Cohen, R. C. *Atmos. Chem. Phys.* **2006**, *6*, 5321.

Research Questions

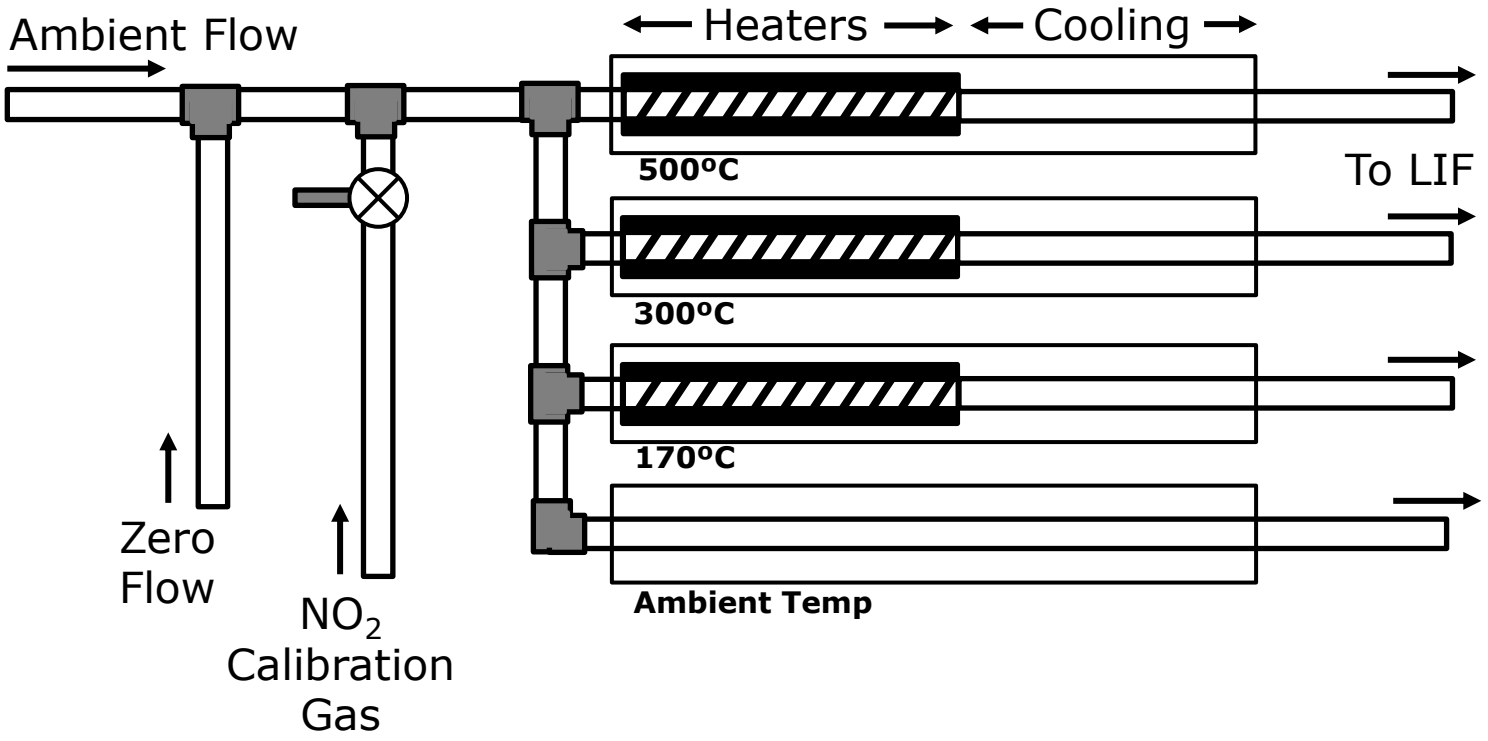


How are NO_x emissions, transport, and chemistry influenced by differences in photochemistry, oxidation, and temperature during the winter?

Thank you for your attention!



TD-LIF detection of nitrogen oxides



- Calibration done using NO_2 standard
- Zero air used to obtain instrument zero

Day, D. A.; Wooldridge, P. J.; Dillon, M. B.; Thornton, J. A.; Cohen, R. C. *J. Geophys. Res.-Atmos.* **2002**, *107*.