Lifetimes of NO_x and its oxidation products during WINTER

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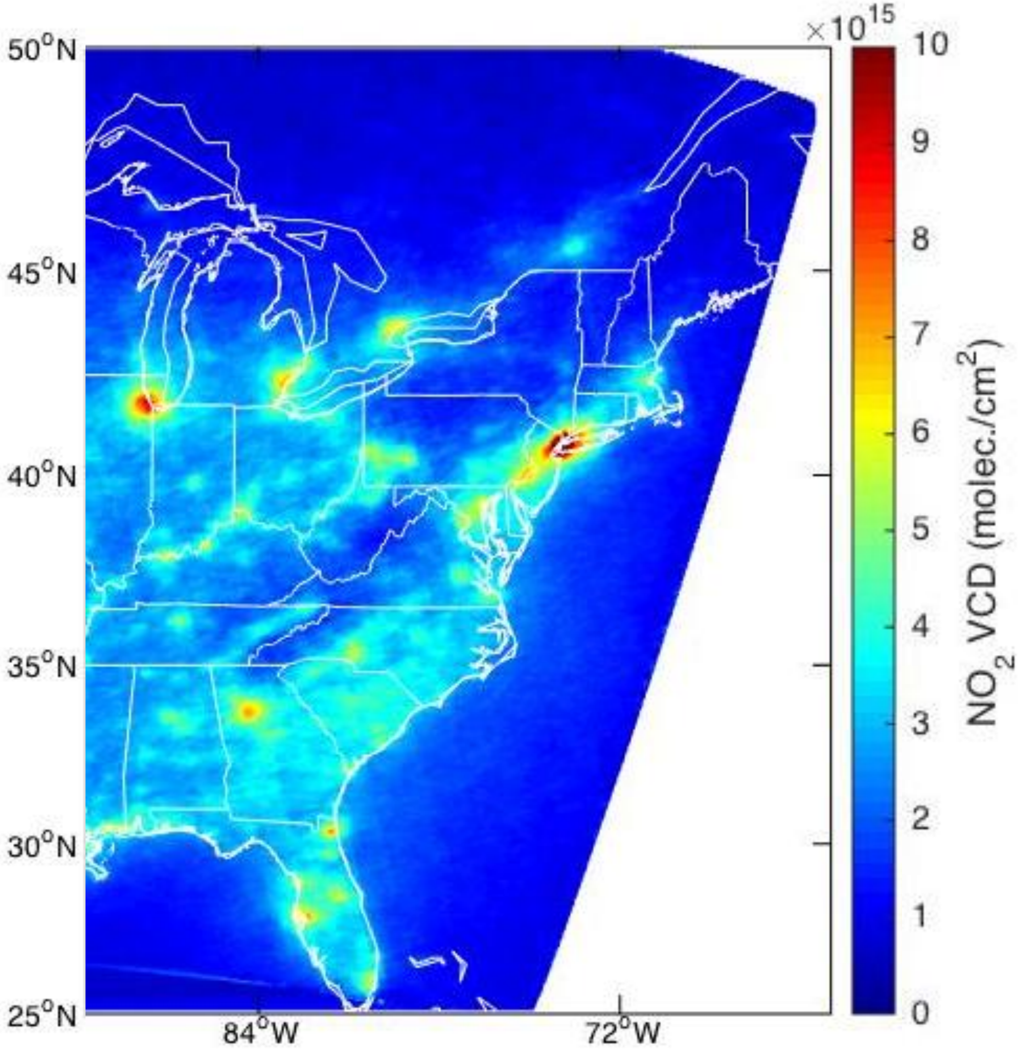
WINTER science meeting
September 17, 2015

Summer 2014 NO_2

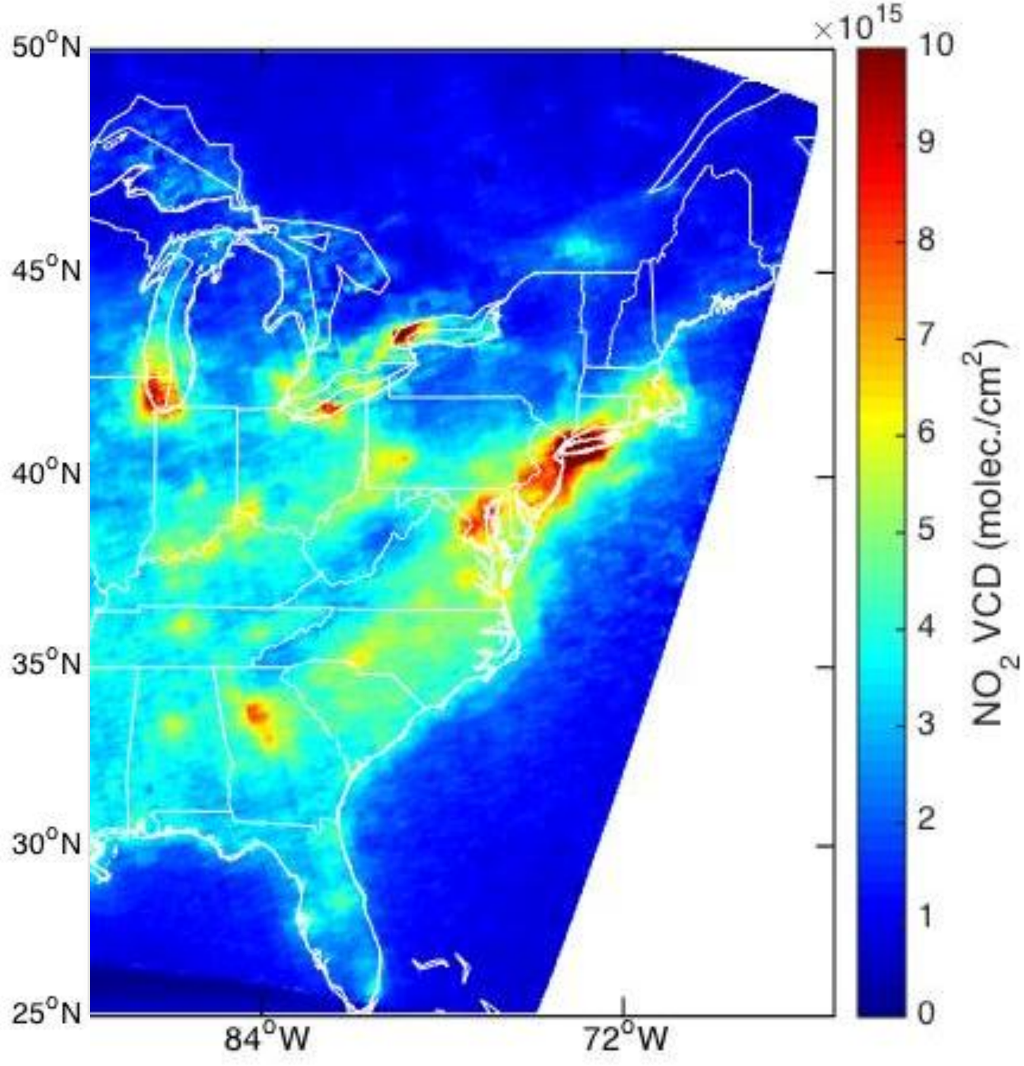
If we assume that an urban plume is 100 km across and that average wind speed is 10 m/s, then NO_x has a lifetime of ~3 hours during summer.



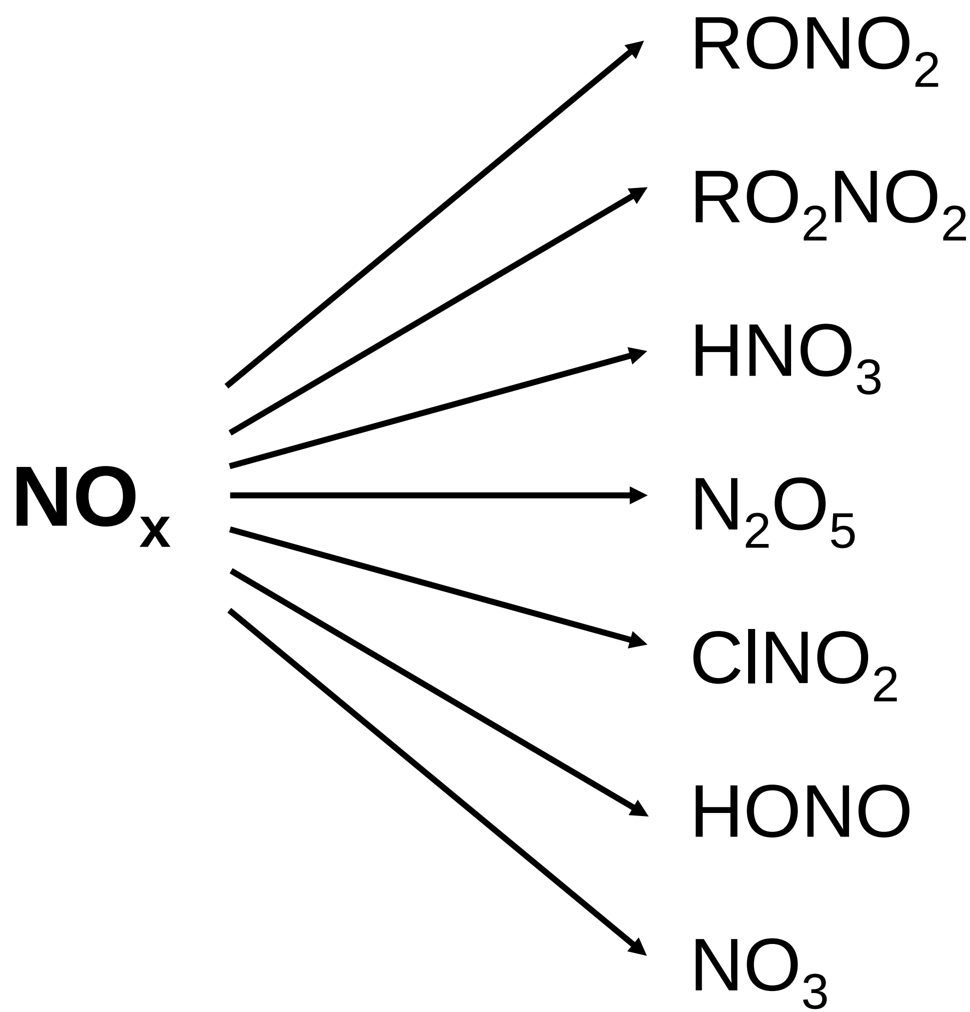
Russell, A. R. et al. *Atmos. Chem. Phys.* **2011**, *11*, 8543.

Winter 2014-15 NO_2

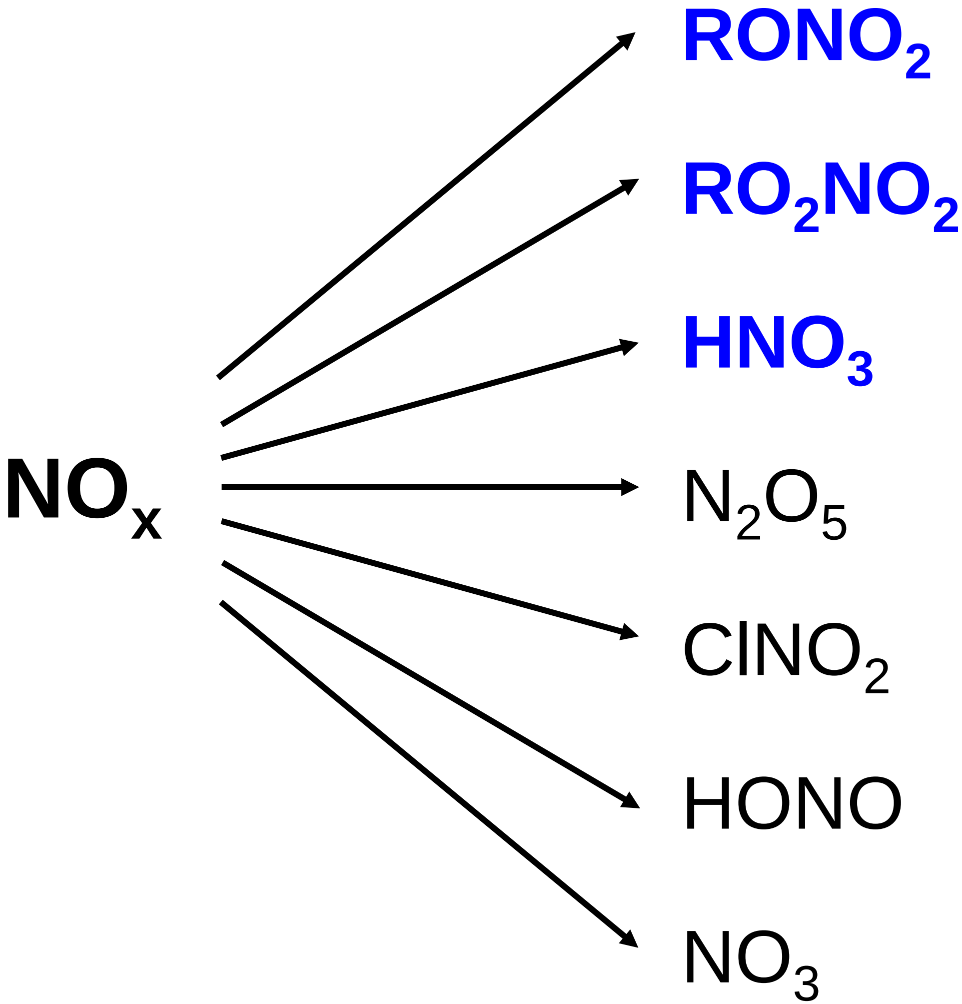
Urban NO_2 plumes are significantly larger and background NO_2 levels are higher in winter, indicating longer NO_x lifetimes.



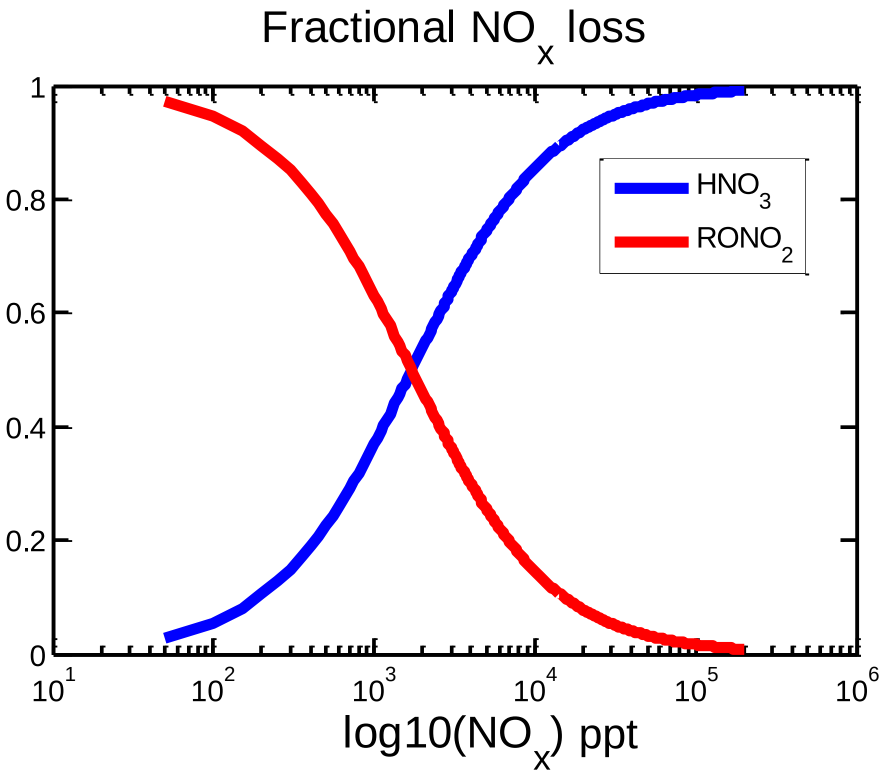
Colder temperatures and longer nights influence the relative balance of NO_x sinks, and therefore NO_x lifetime, during winter.



Colder temperatures and longer nights influence the relative balance of NO_x sinks, and therefore NO_x lifetime, during winter.



NO_x concentrations influence relative partitioning of sinks



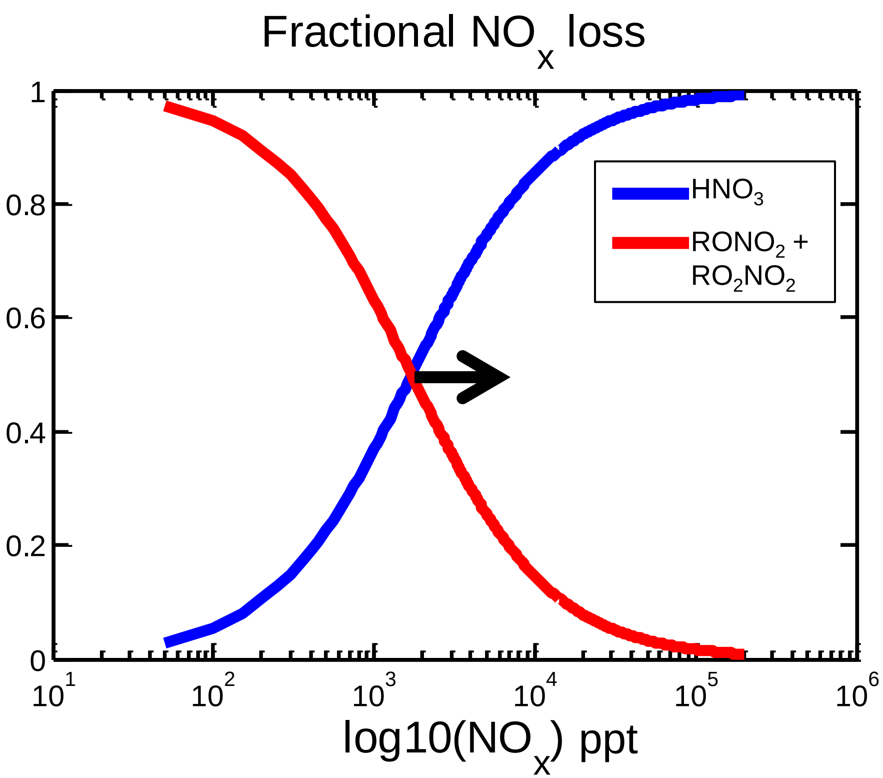
Simplest case: summer daytime

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

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

Browne, E. C. et al. *Atmos. Chem. Phys.* **2013**, *13*, 4543.

NO_x concentrations influence relative partitioning of sinks



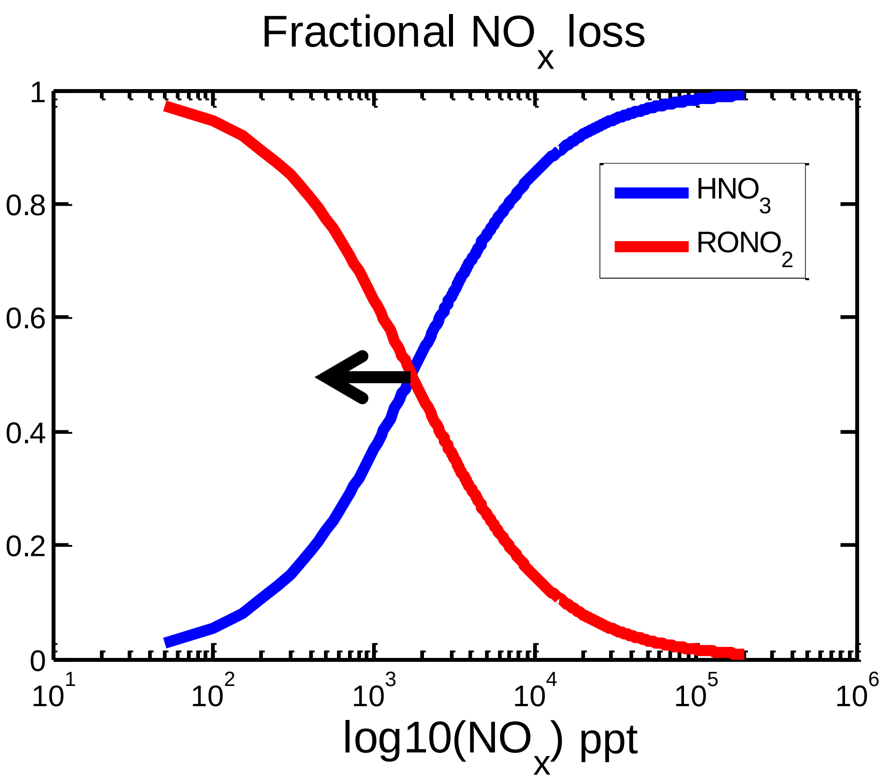
$$NO_2 + OH \xrightarrow{M} HNO_3$$

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

In winter, peroxy nitrate lifetimes are longer:

$$RO_2 + NO_2 \xrightarrow{M} RO_2NO_2$$

NO_x concentrations influence relative partitioning of sinks



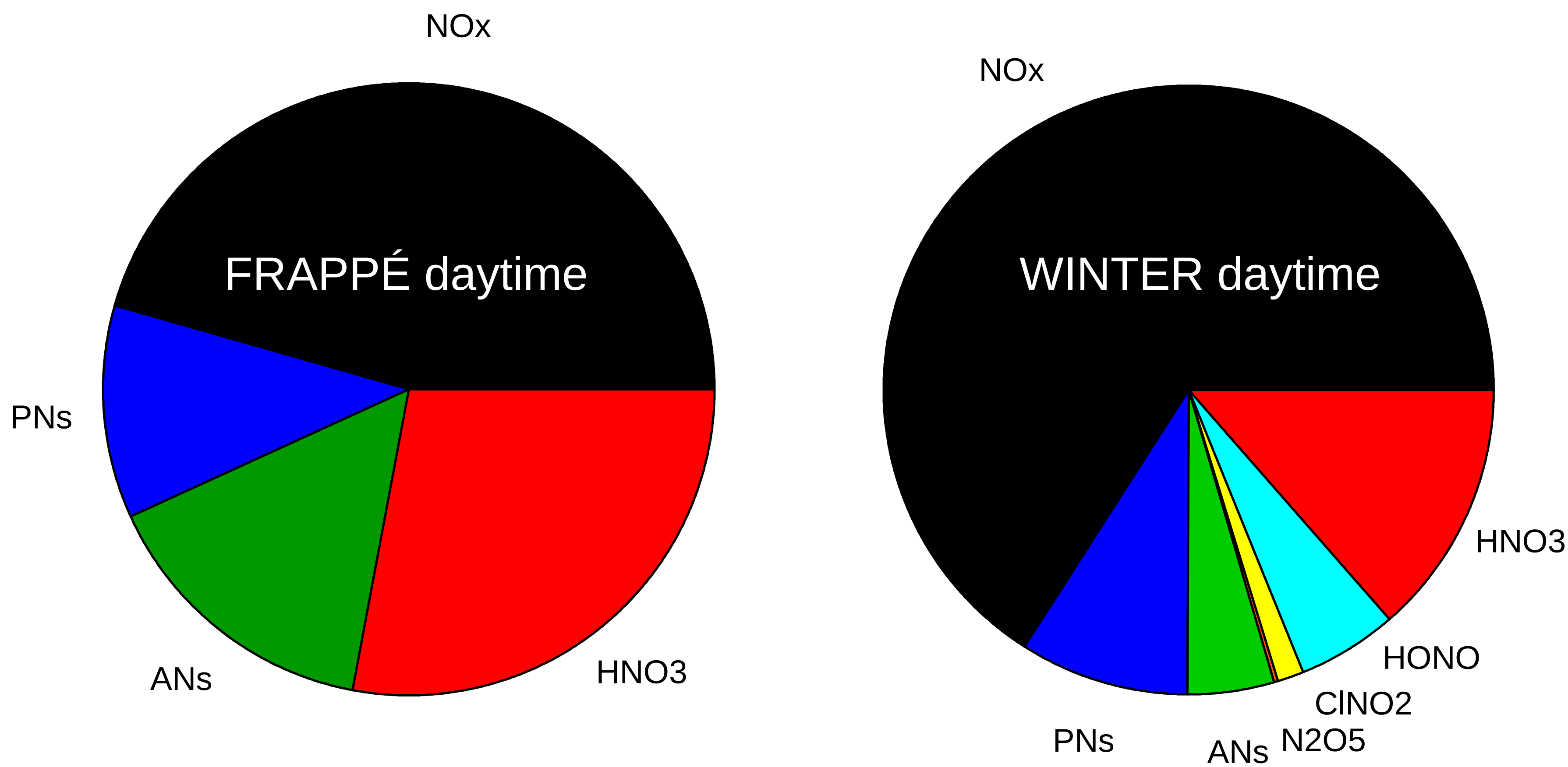
$$NO_2 + OH \xrightarrow{M} HNO_3$$

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

At night:

$$N_2O_5 + H_2O \xrightarrow{M} 2HNO_3$$

NO_y in summer vs. winter

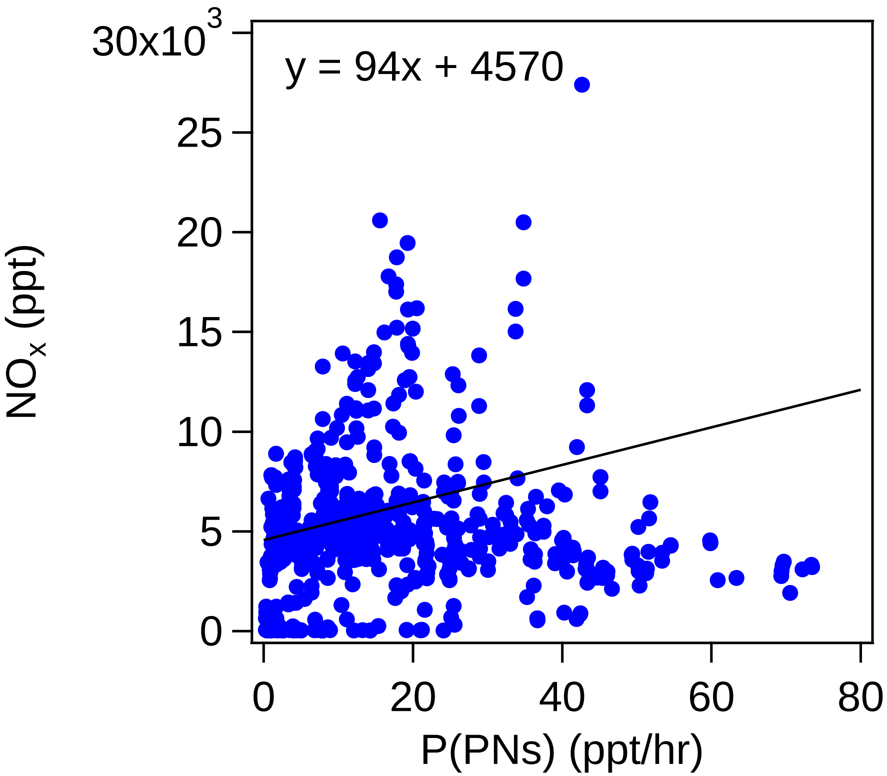


What is the lifetime of NO_x with respect to each of its various sinks?

P(ΣPNs) and impact on τ_{NOx}

$$\beta = \frac{k_{PA+NO2}[NO_2]}{k_{PA+NO2}[NO_2] + k_{PA+NO}[NO] + k_{PA+HO2}[HO_2] + k_{PA+RO2}[RO_2]}$$

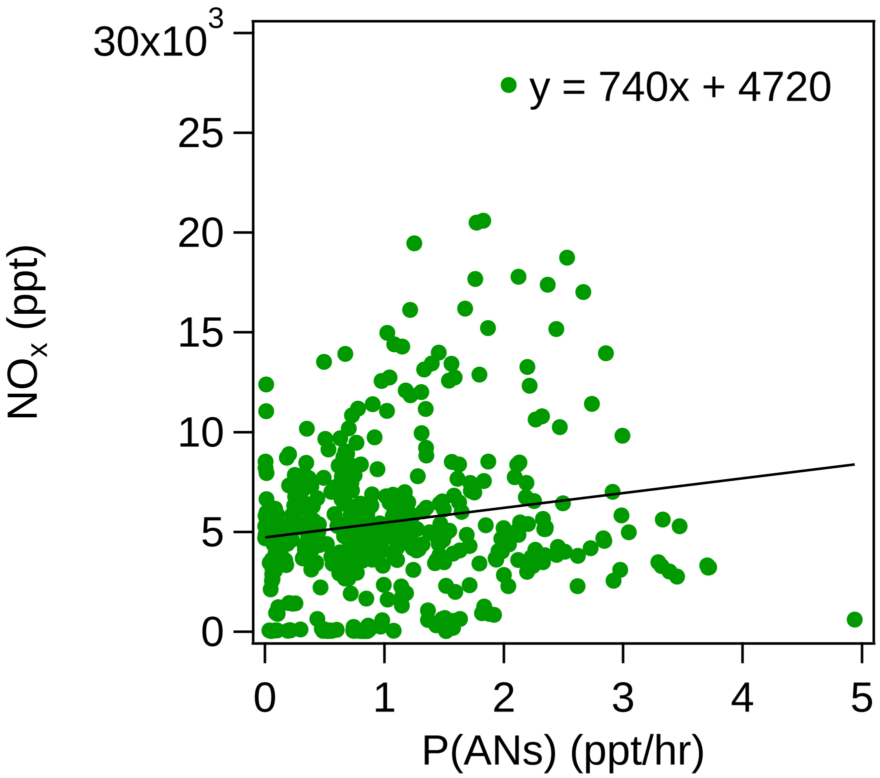
$$P(\Sigma PNs) = \beta \cdot \alpha_{CH3CHO} \cdot k_{CH3CHO}\,[OH][CH_3CHO]$$



$\tau_{NOx,PNs}$ = 94 hrs

LaFranchi, B. W. et al. *Atmos. Chem. Phys.* **2009**, *9*, 7623.

P(ΣANs) and impact on τ_{NOx}



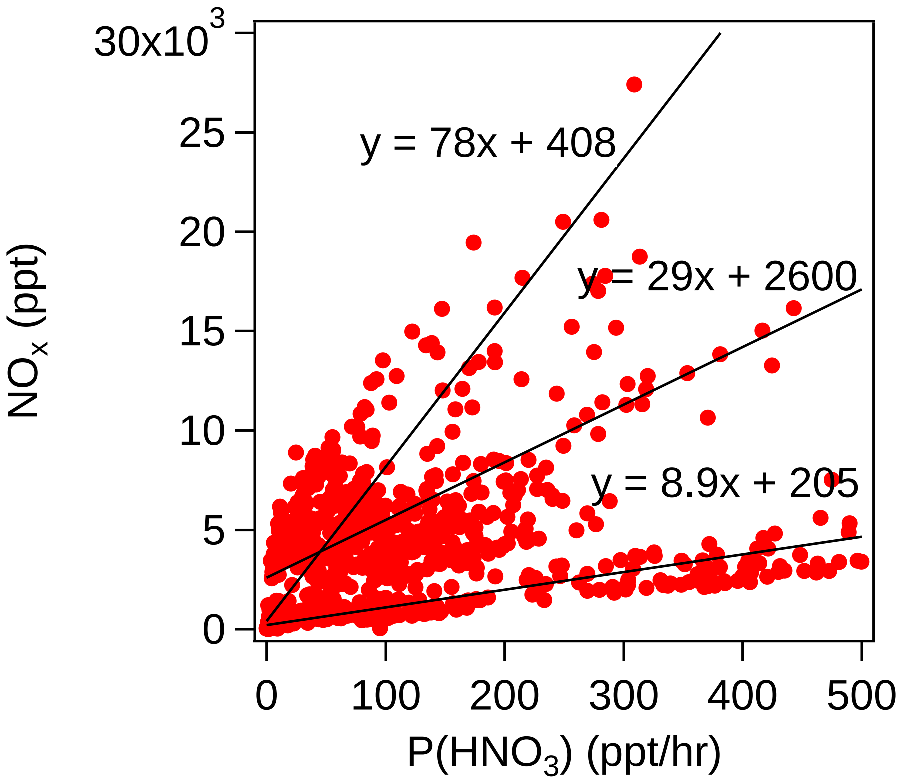
$$RO_2 + NO \xrightarrow{M} RONO_2$$

$$P(\sum_i ANs) = \sum_i (\alpha_i \cdot k_{VOC,i+OH} \cdot [VOC]_i)[OH]$$

$\tau_{NOx,ANs}$ = 740 hrs

Perring, A. E.; Pusede, S. E.; Cohen, R. C. *Chem. Rev.* **2013**, *113*, 5848.
Farmer, D. K. et al. *Atmos. Chem. Phys.* **2011**, *11*, 4085.
Rosen, R. S. et al. *J. Geophys. Res.-Atmos* **2004**, *109*.

$P(HNO_3)$ and impact on τ_{NOx}



During the day:

$$P(HNO_3) = k_{OH+NO2}[OH][NO_2]$$

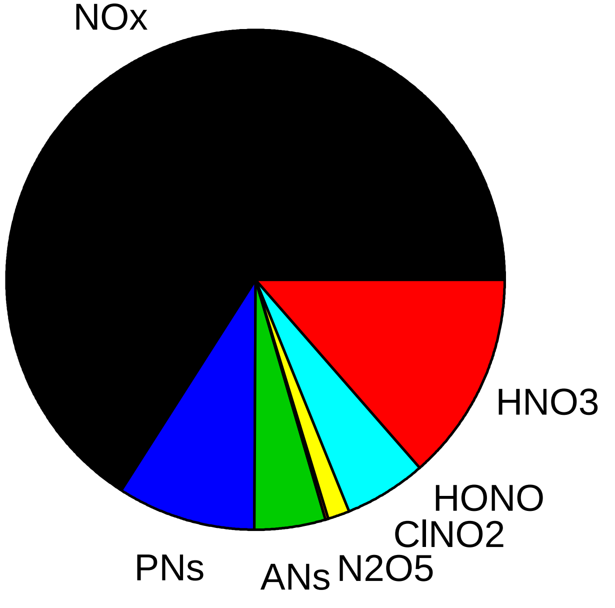
Different chemical environments – but all NO_x lifetimes are shorter than those due to PNs or ANs

τ_{NOx}

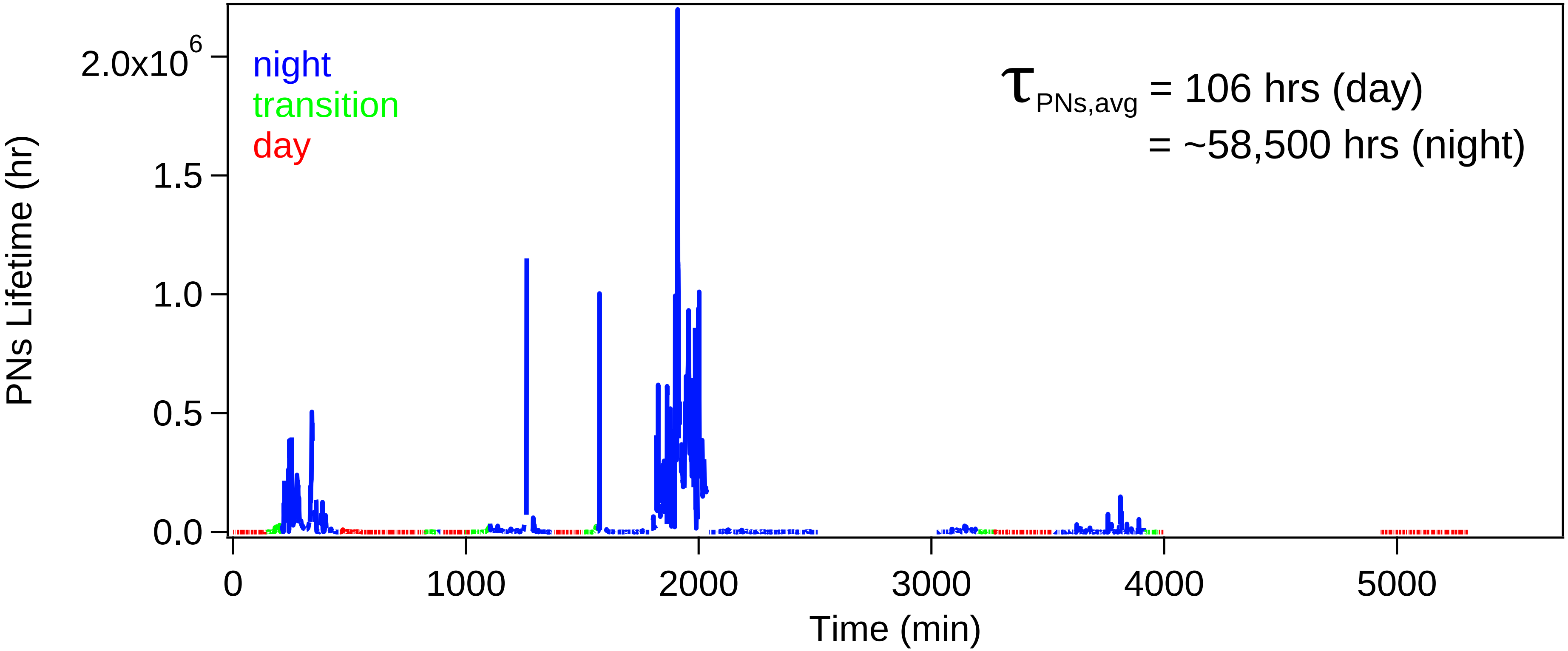
Production of HNO_3 has by far the largest influence on τ_{NOx}. Yet, the fraction of NO_y composed of HNO_3 vs. ΣPNs + ΣANs is similar.

We have to consider local vs. global photochemistry.

How is the idea of local vs. global (or near field vs. far field) chemistry reflected in the fate of NO_x sinks?



τ_{PNs} during WINTER



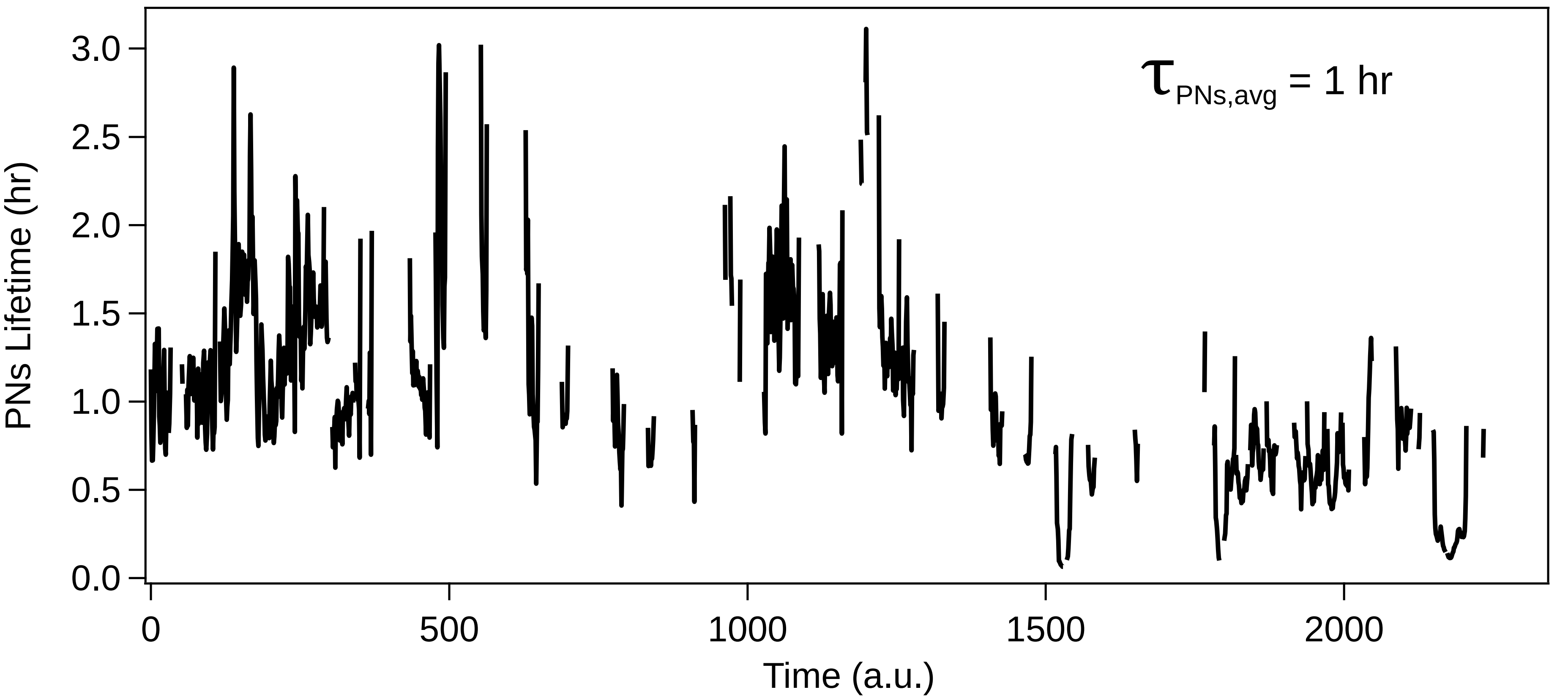
$$RC(O)OO + NO_2 \rightleftharpoons RC(O)OONO_2 \qquad (1)$$

$$CH_3C(O)OO + NO \rightarrow CH_3C(O)O + NO_2 \quad (2)$$

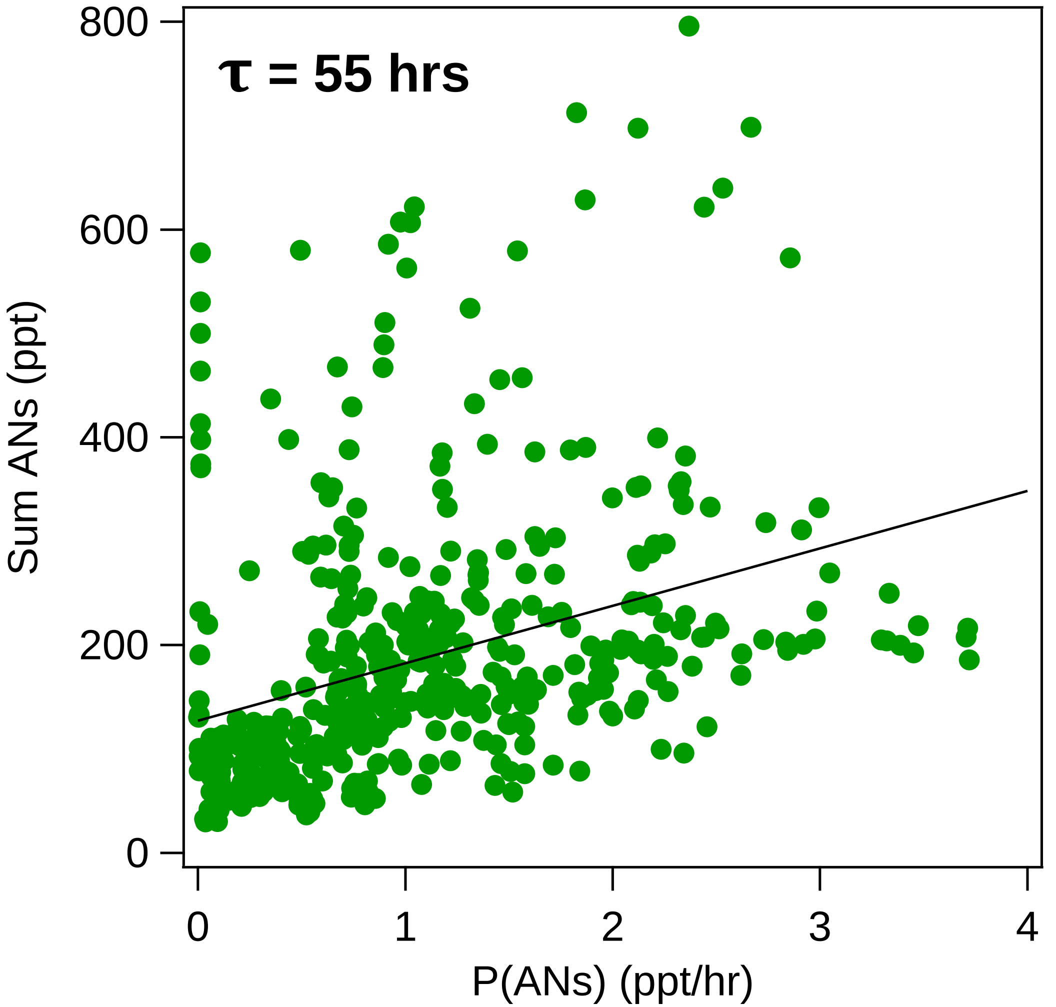
$$\tau_{PNs} = \frac{1}{k_{1r}}\left(1 + \frac{k_{1f}[NO_2]}{k_2[NO]}\right)$$

Wolfe, G. M. et al. *Atmos. Chem. Phys.* **2009**, *9*, 615.
Turnipseed, A. A. et al. *J. Geophys. Res.-Atmos* **2006**, *111*.

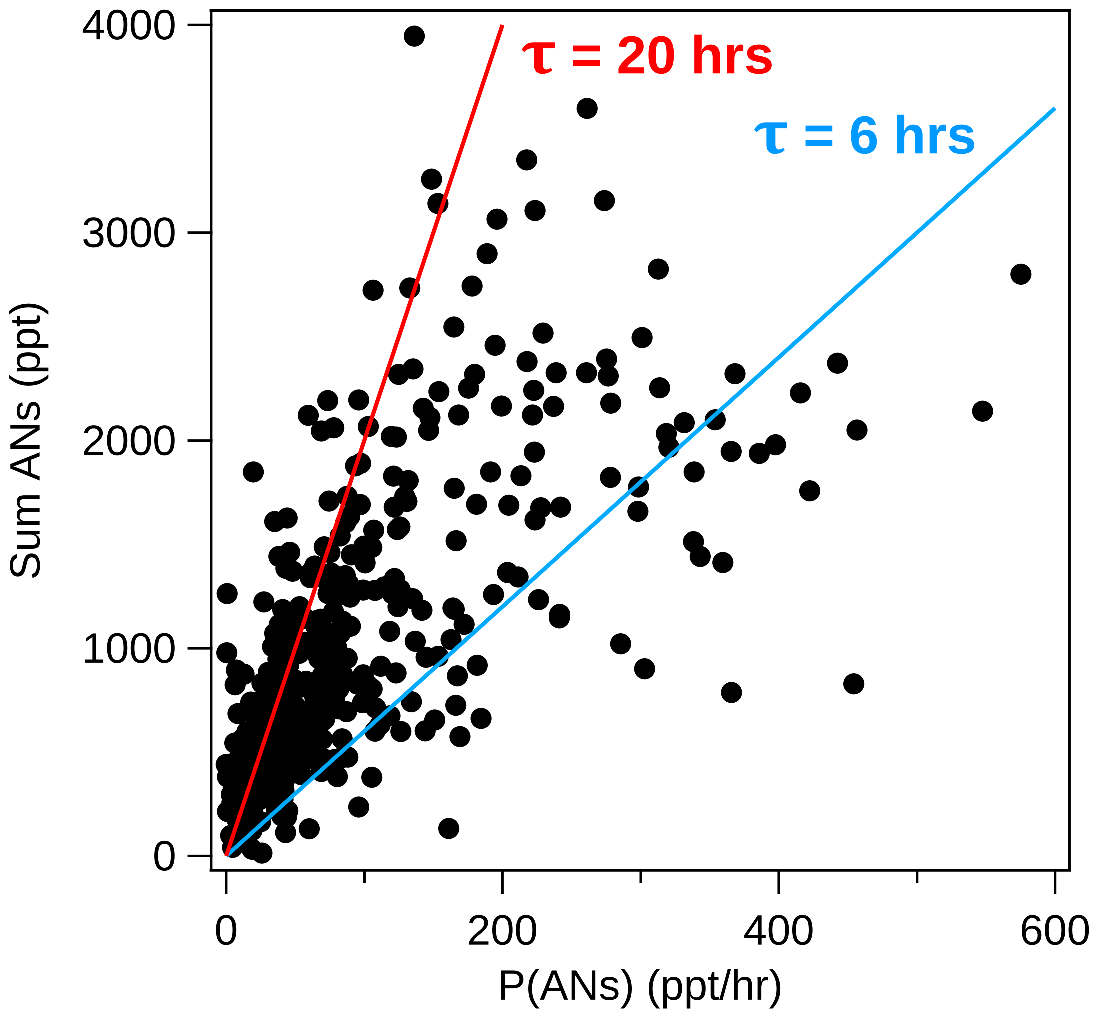
τ_{PNs} during summer



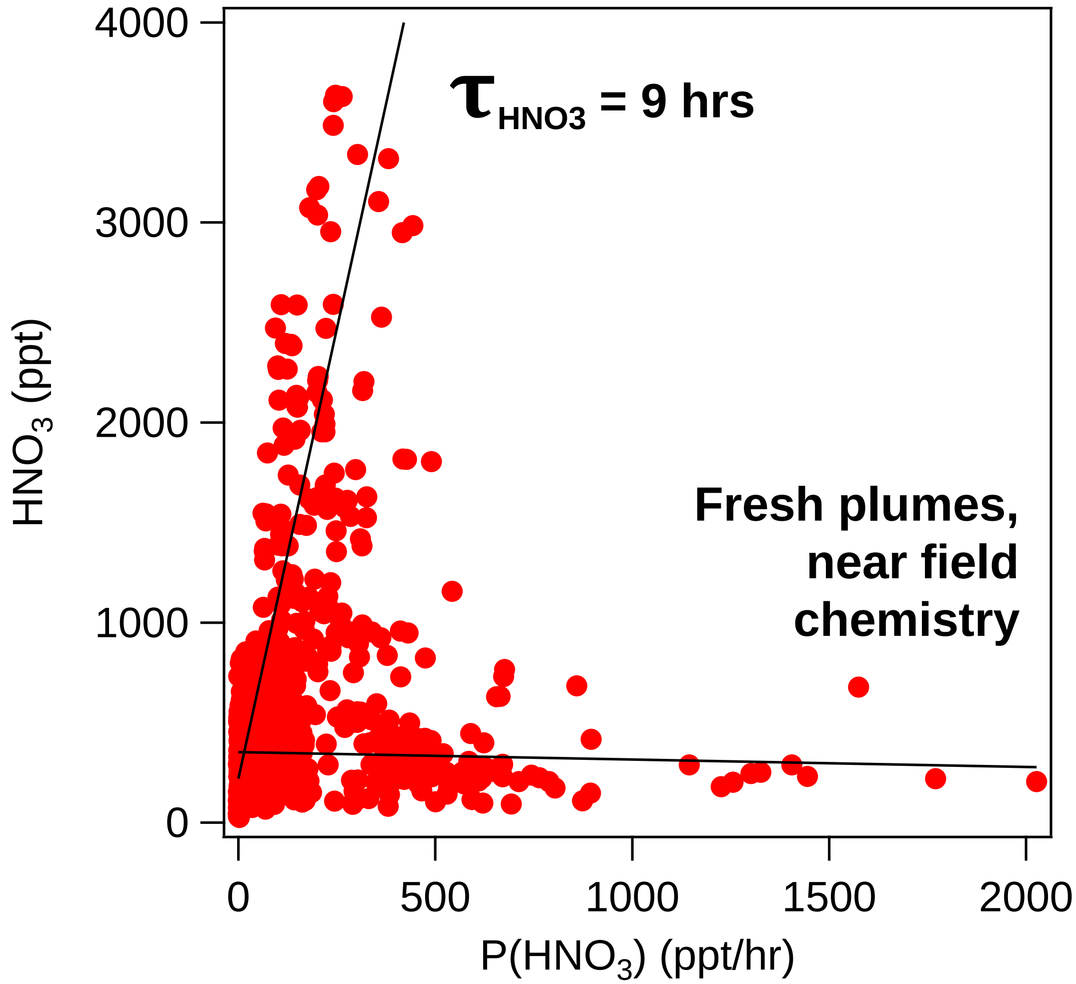
τ_{ANs} during winter daytime



τ_{ANs} during summer



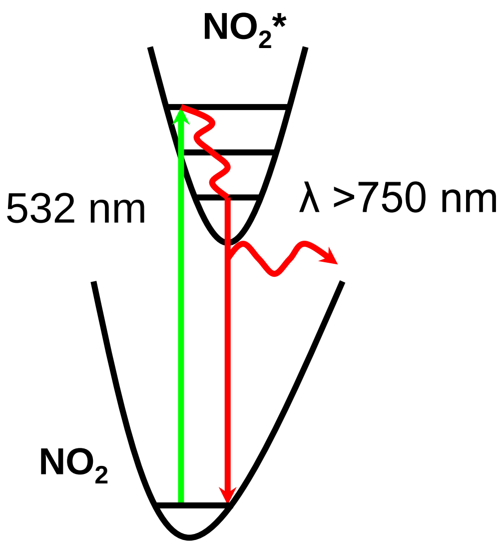
τ_{HNO3} during winter daytime

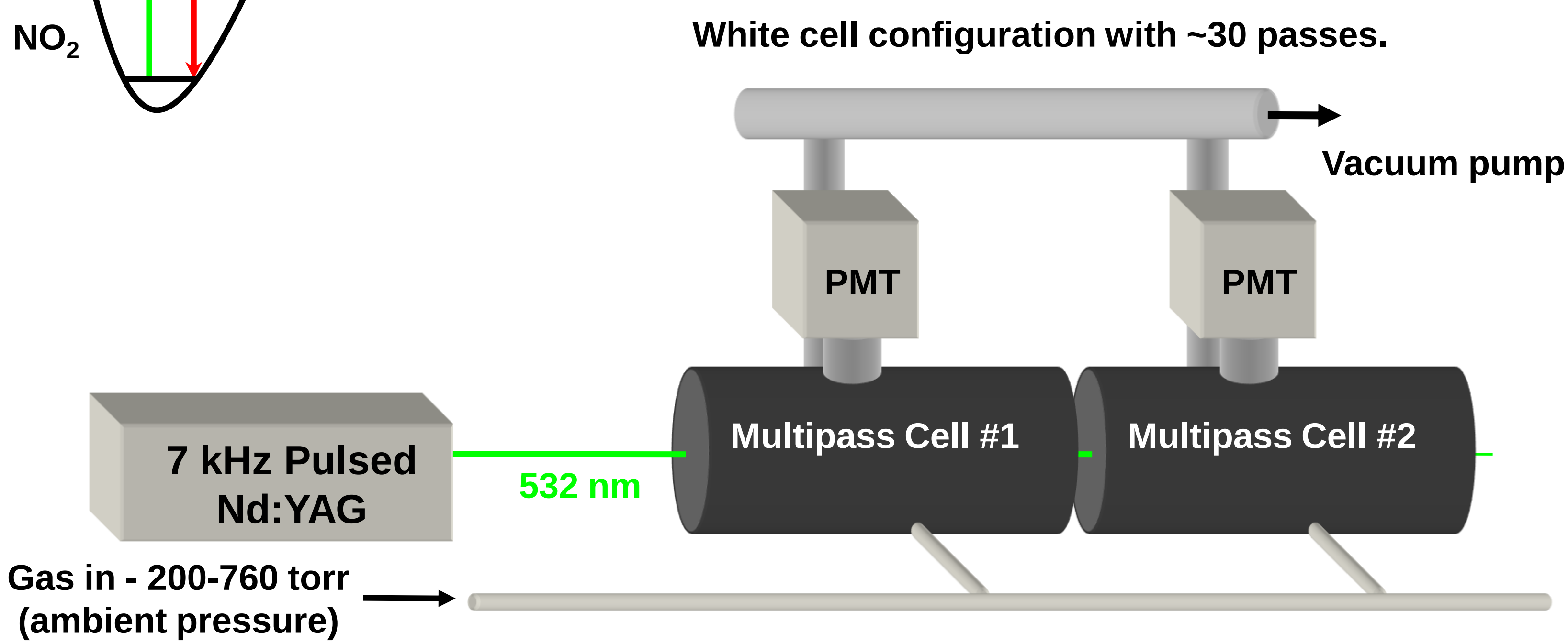


Questions

- How do the lifetimes of NO_x and $NO_{y,i}$ vary in the near and far field?
- What is the role of N_2O_5 and chlorine chemistry in regulating the lifetime of NO_x?
- How do NO_x emissions and subsequent oxidation chemistry affect the oxidant balance in winter, and over what scales do these effects extend?

Laser-induced fluorescence (LIF) detection of NO_2

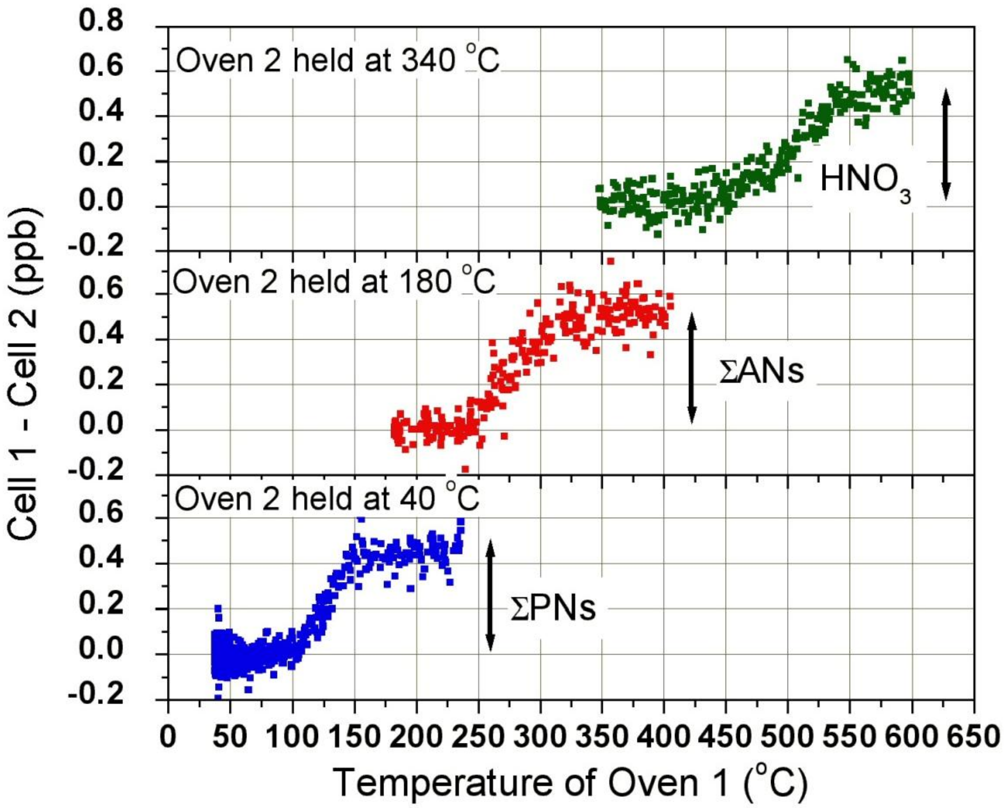


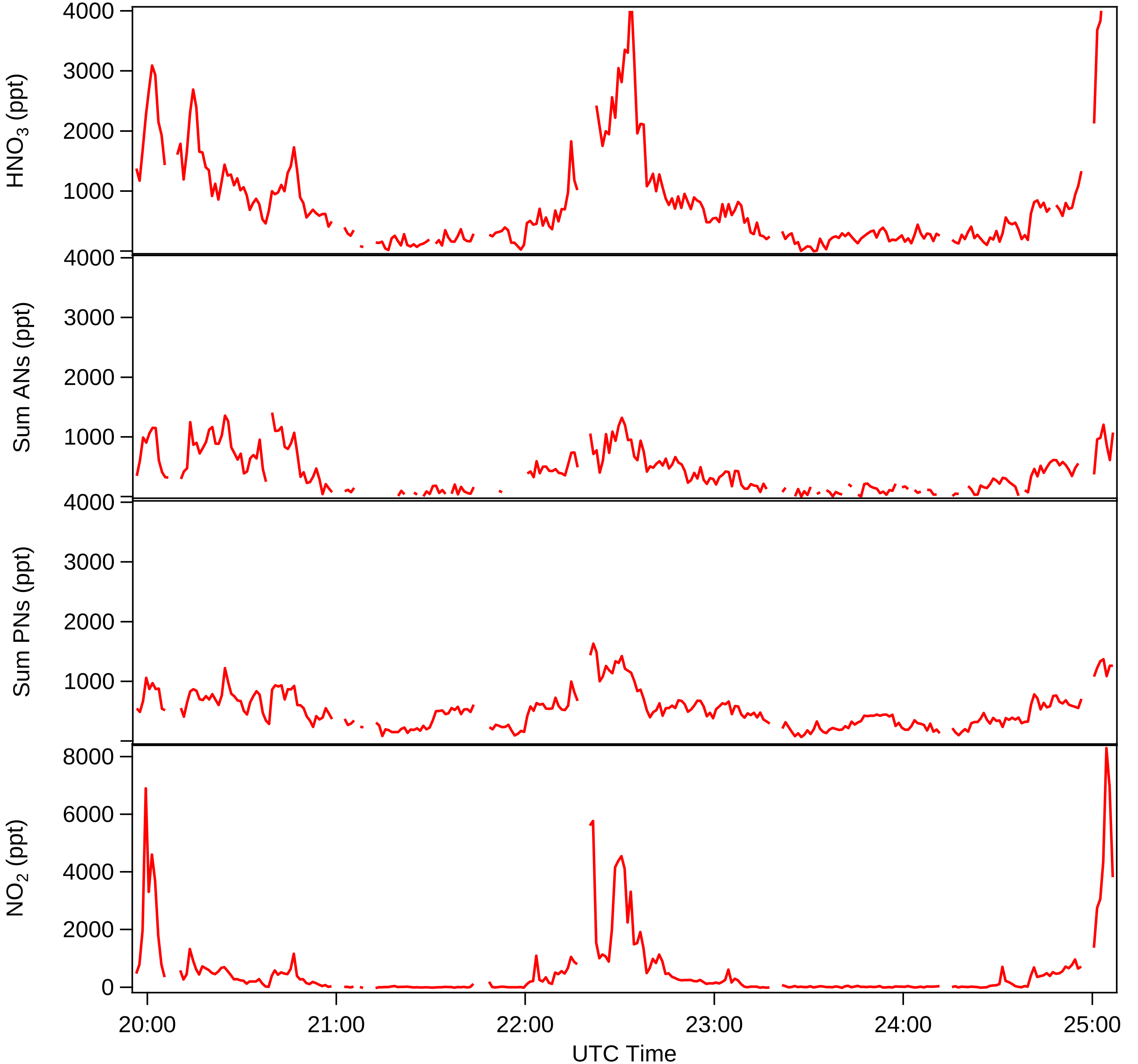


Thornton, J. A.; Wooldridge, P. J.; Cohen, R. C. *Anal. Chem.* **2000**, *72*, 528.
Bertram, T. H.; Perring, A. E.; Wooldridge, P. J.; Dibb, J.; Avery, M. A.; Cohen, R. C. *Atmos. Chem. Phys.* **2013**, *13*, 4617.

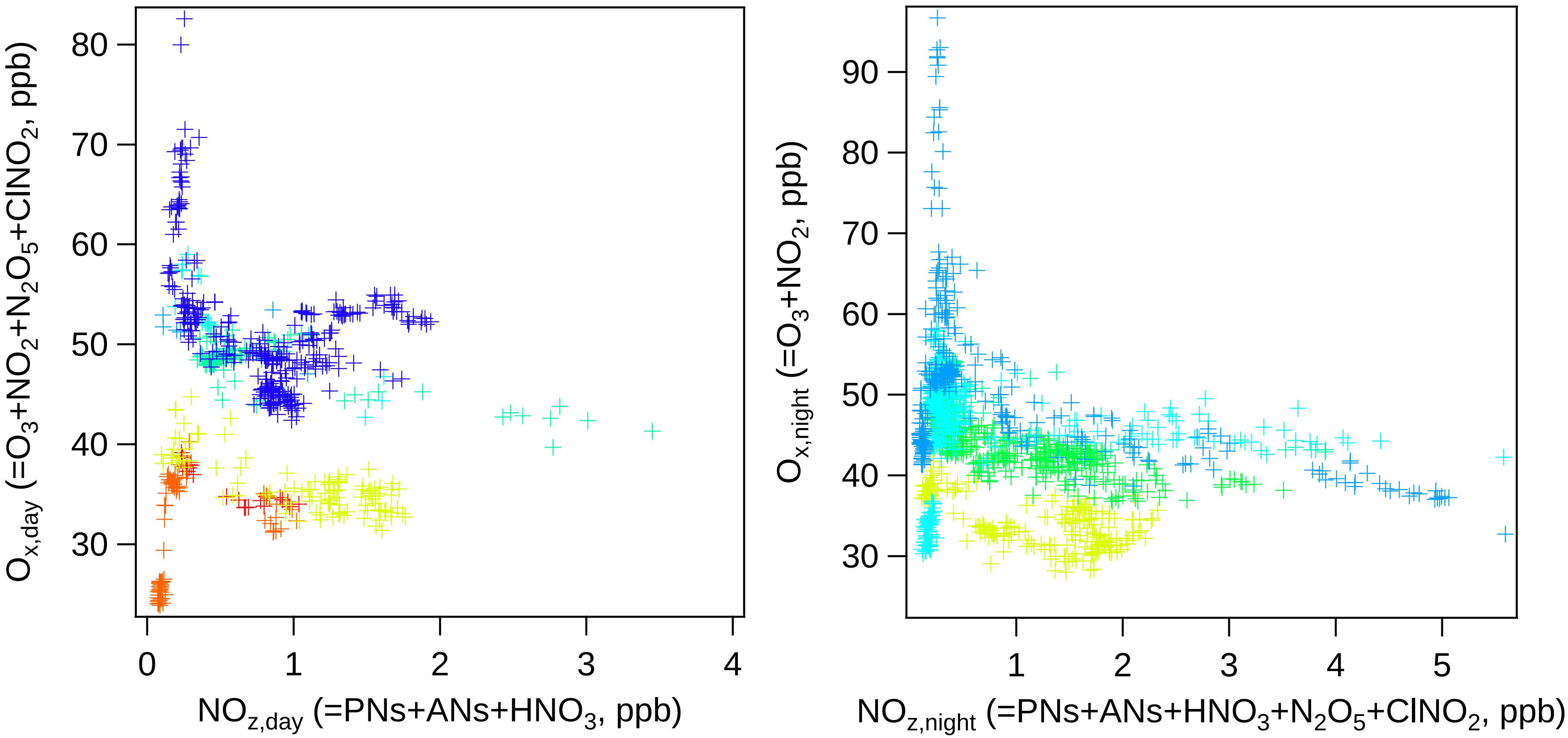
Thermal dissociation laser-induced fluorescence (TD-LIF)

- 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.

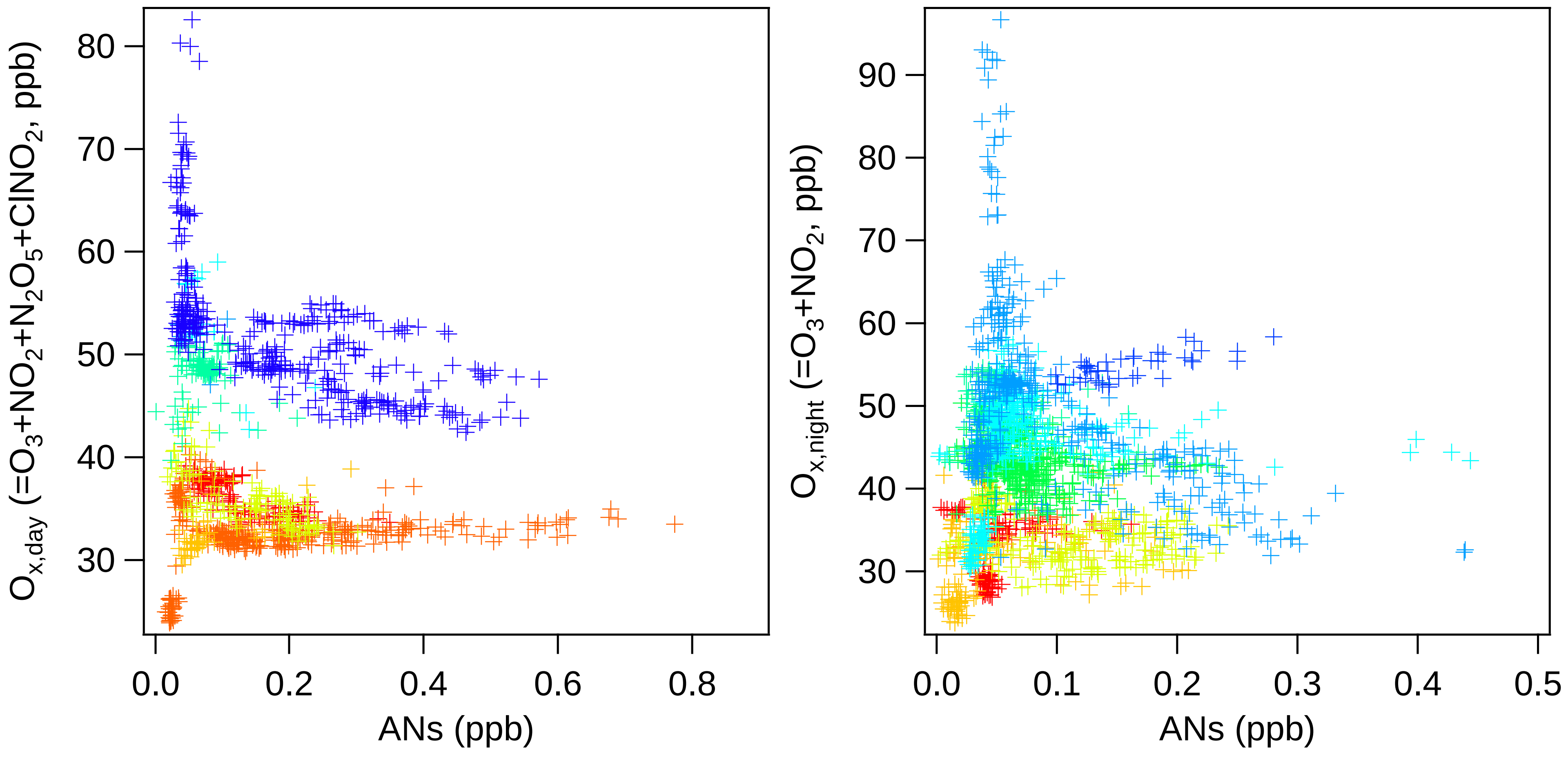




HNO3 (ppt)
Sum ANs (ppt)
Sum PNs (ppt)
NO2 (ppt)
4000
3000
2000
1000
8000
6000
4000
2000
0
20:00
21:00
22:00
23:00
24:00
25:00
UTC Time



80
70
60
50
40
30
O_x,day (=O_3+NO_2+N_2O_5+ClNO_2, ppb)
0
1
2
3
4
NO_z,day (=PNs+ANs+HNO_3, ppb)
90
80
70
60
50
40
30
O_x,night (=O_3+NO_2, ppb)
1
2
3
4
5
NO_z,night (=PNs+ANs+HNO_3+N_2O_5+ClNO_2, ppb)



$O_{x,day}$ (=O_3+NO_2+N_2O_5+$ClNO_2$, ppb)
80
70
60
50
40
30
0.0
0.2
0.4
0.6
0.8
ANs (ppb)
$O_{x,night}$ (=O_3+NO_2, ppb)
90
80
70
60
50
40
30
0.0
0.1
0.2
0.3
0.4
0.5
ANs (ppb)