Long-term observations of nitrate radicals at a semiarid urban site

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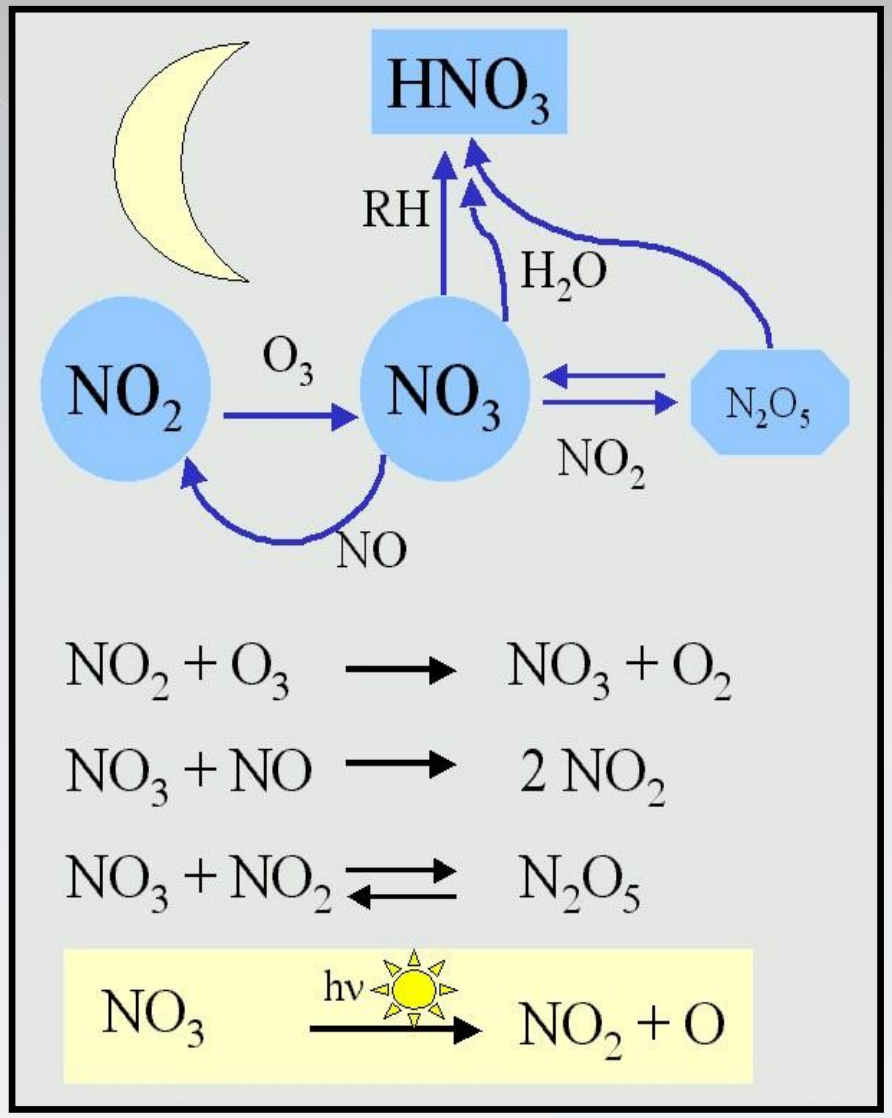
NO_3

- The NO_3 makes an important contribution to the oxidizing capacity of the troposphere (second to OH radical)
- Plays a role as a nighttime sink for NO_x
- Reacts with a number of VOC's initiating their night time degradation
- Plays a major role in the conversion of NO_x to reservoirs N_2O_5 and HNO_3 through a non-photochemical process

Nighttime Chemistry



Objectives

- Describe seasonal and spatial **patterns** in the behavior of the nitrate radical

- Document NO_3 **interaction** with other tropospheric gases under the current conditions and evaluate the contribution of its **different sinks**

- Evaluate its **oxidation potential** and contribution to the transformation and removal of atmospheric compounds

Light path employed by:

- **HUJI DOAS**
- **HEID DOAS**

$$c = \frac{D(\lambda)}{\sigma(\lambda) \cdot L}$$

Trace gases: -

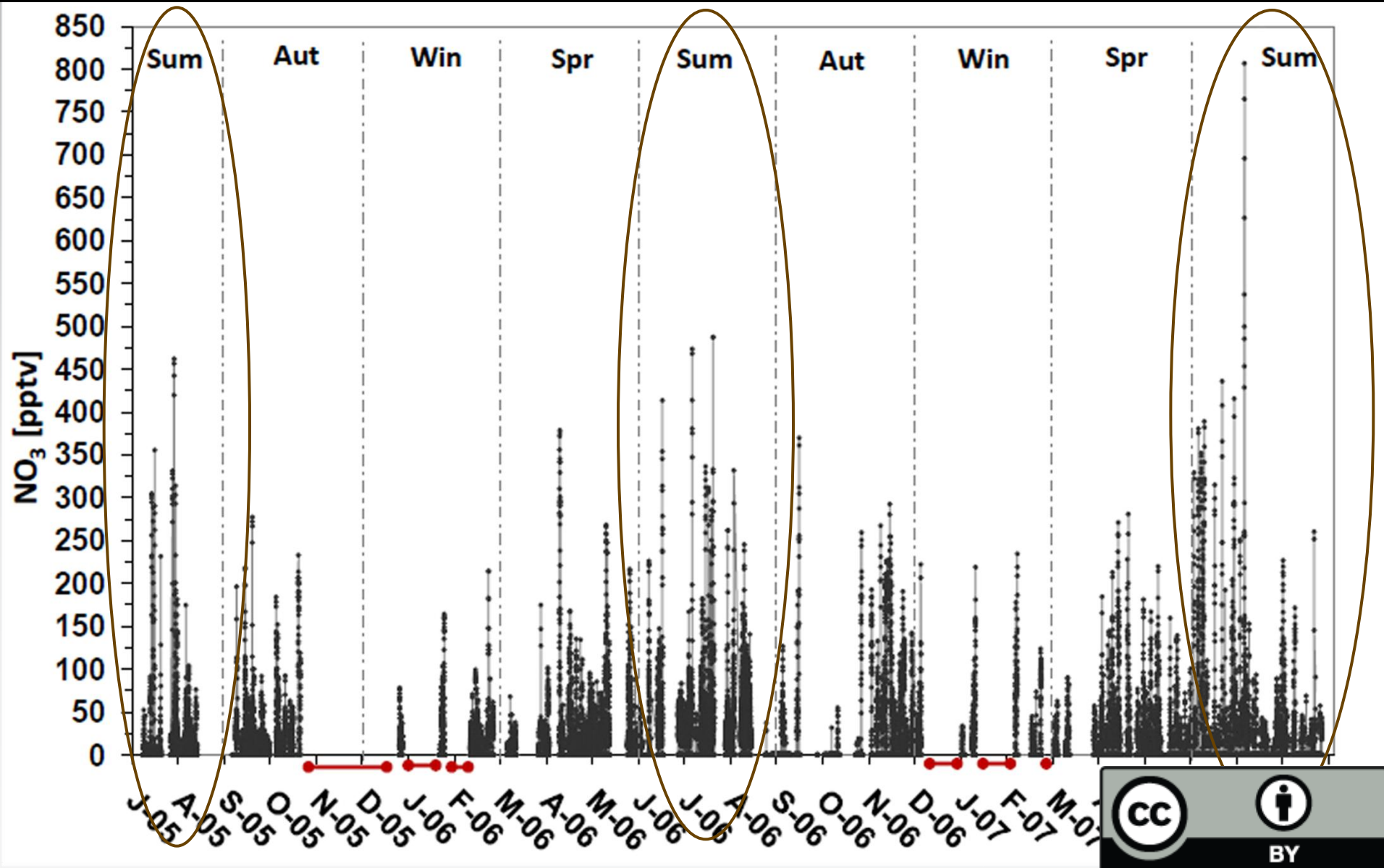
- NO/NO_x*
- O_3

Meteorology:

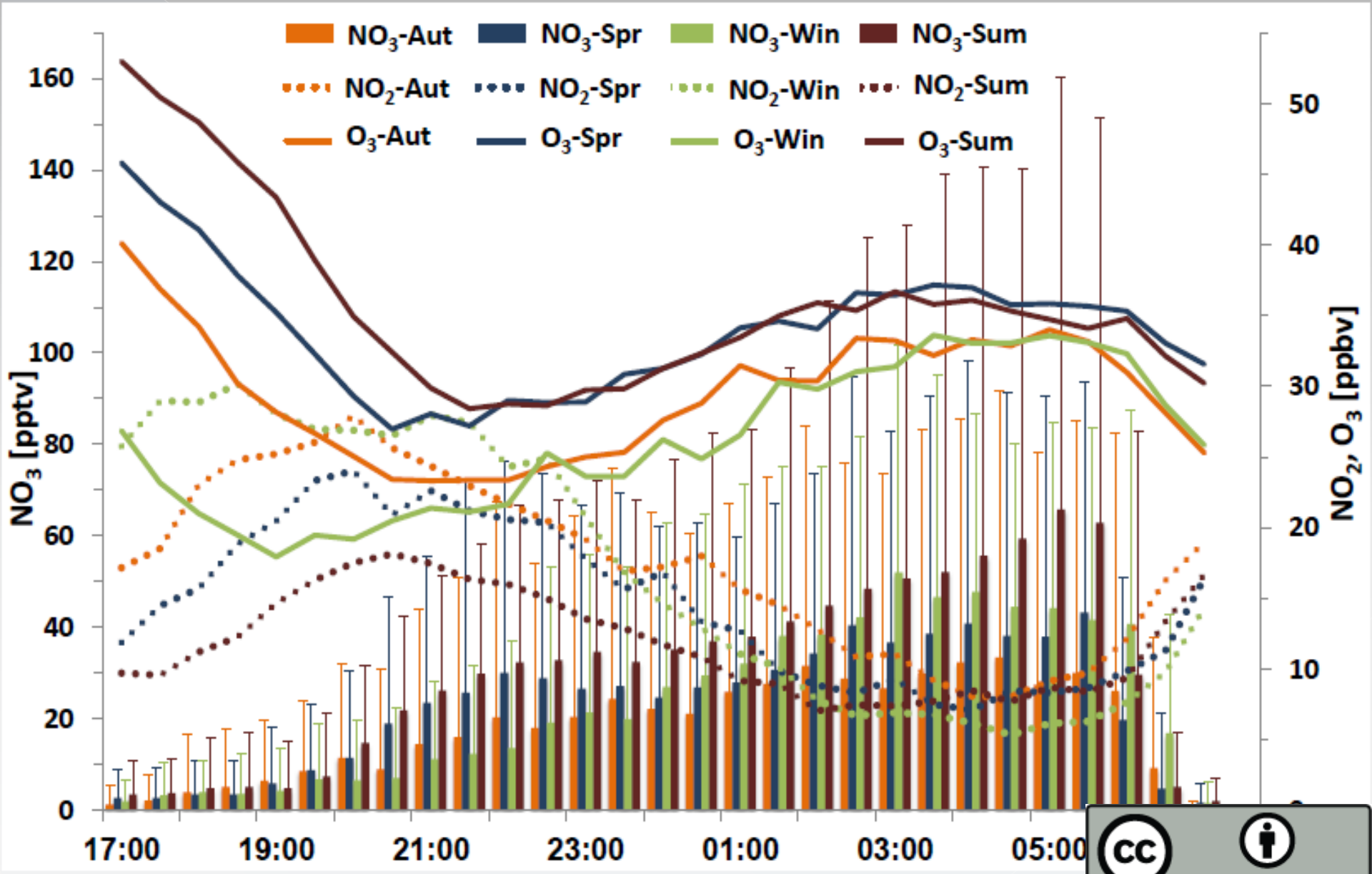
- Temp
- RH
- WDS - WDD
- Pressure
- Solar Radiation

Time series

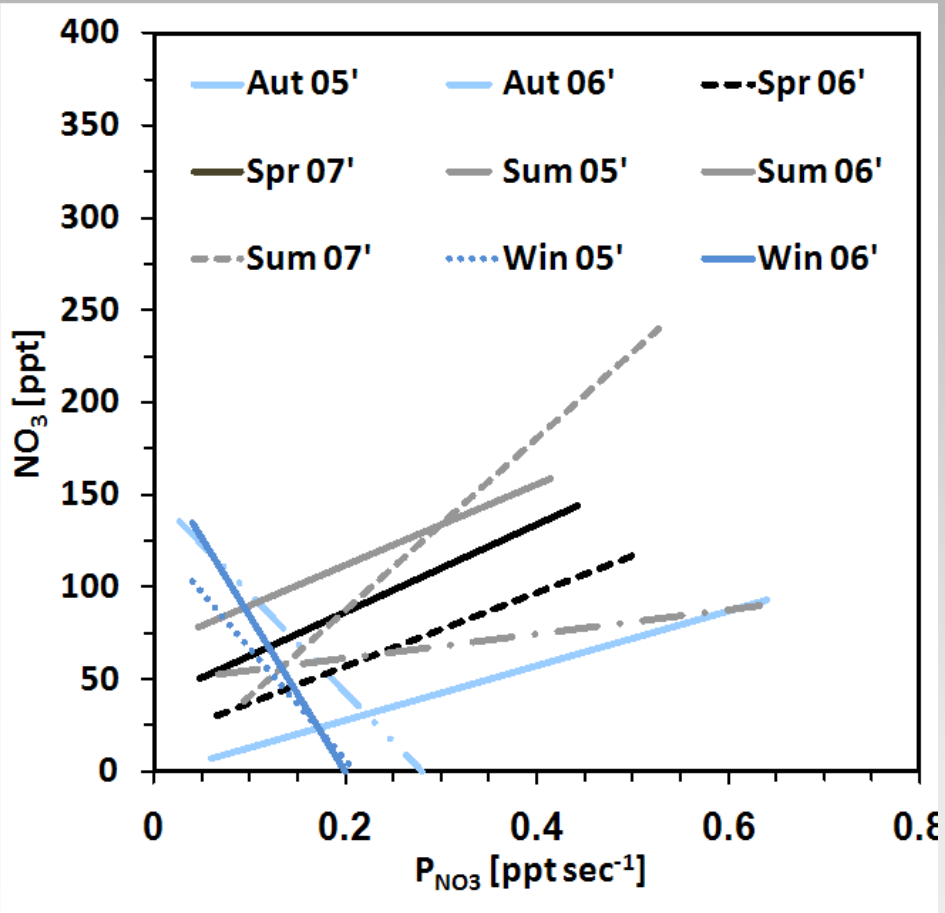
Avg: 27.3±43.5 **ppt**



Diurnal analysis

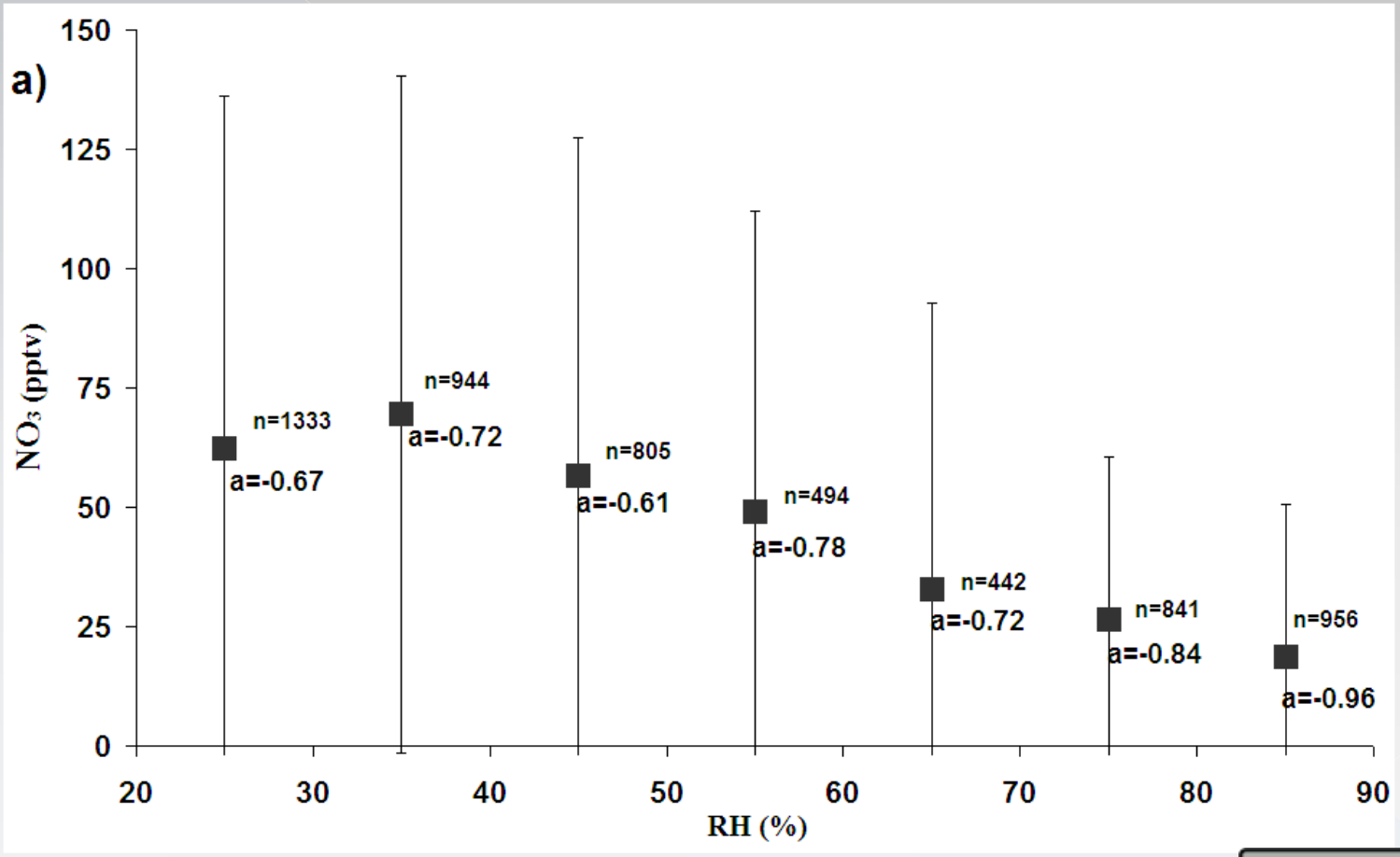


Correlation studies as indicator of the major NO_3 removal path: $[NO_3]$ vs. P_{NO3}



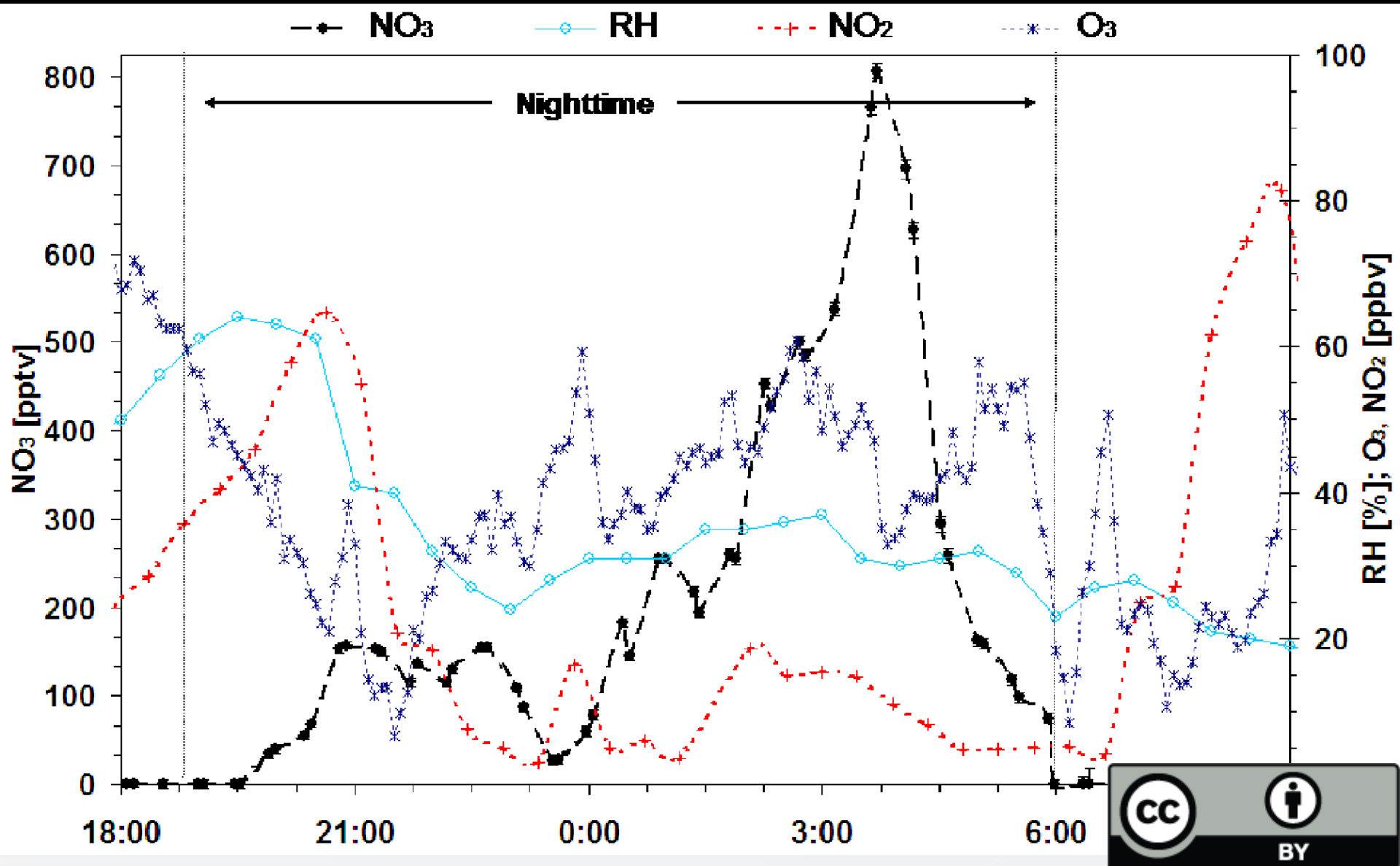
Season	Direct loss indicators $[NO_3] = a \times (P_{NO3}) + b$ (R^2)	τNO_3 due to effect of dir. losses (min)	Indirect loss indicators $\ln(\tau(NO_3)) = -a \times \ln[NO_2] + b$ (R^2)	τNO_3 due to effect of indir. losses (min)
Campaign	$y = 458.7x - 37.2(0.27)$	3.3	$y = -0.6x + 6.8(0.34)$	7.8

Relative humidity Vs. NO_3

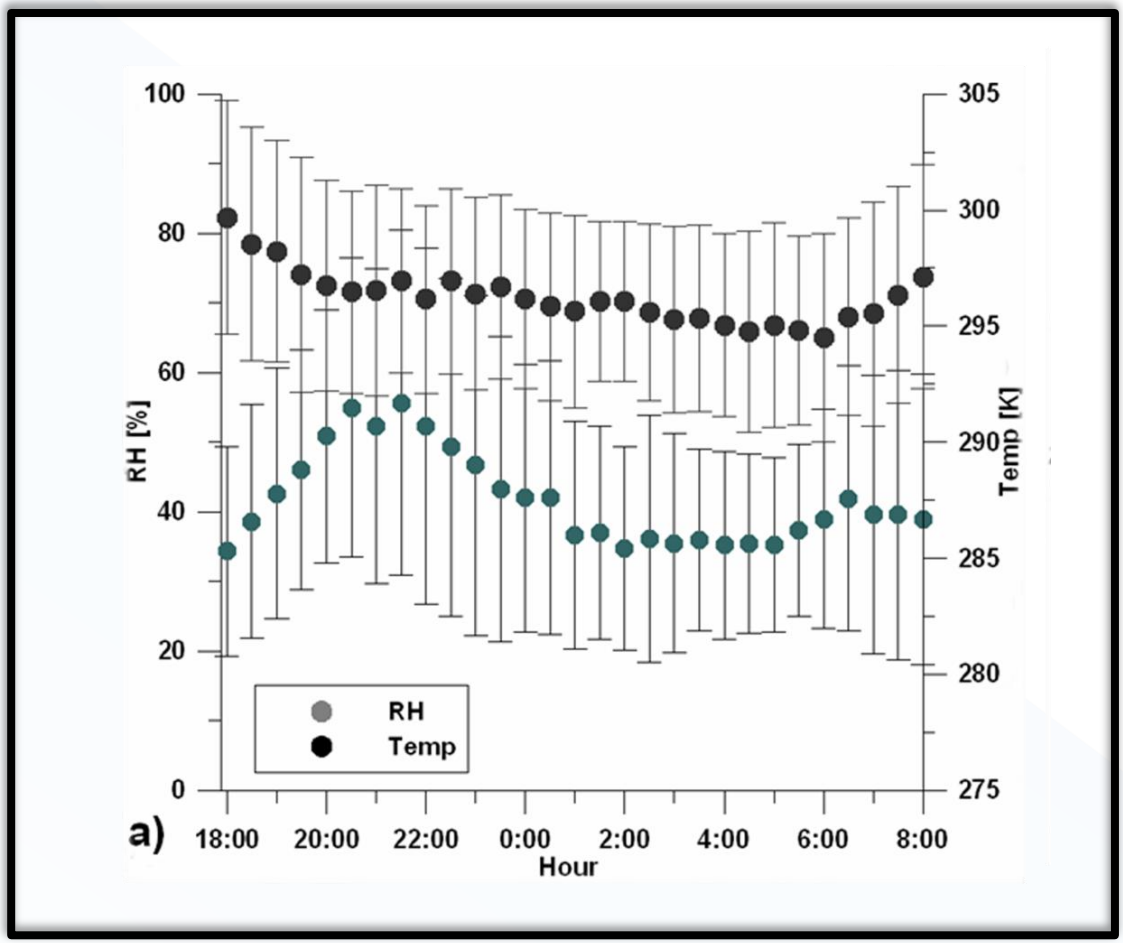


Highest levels of NO_3 ever reported

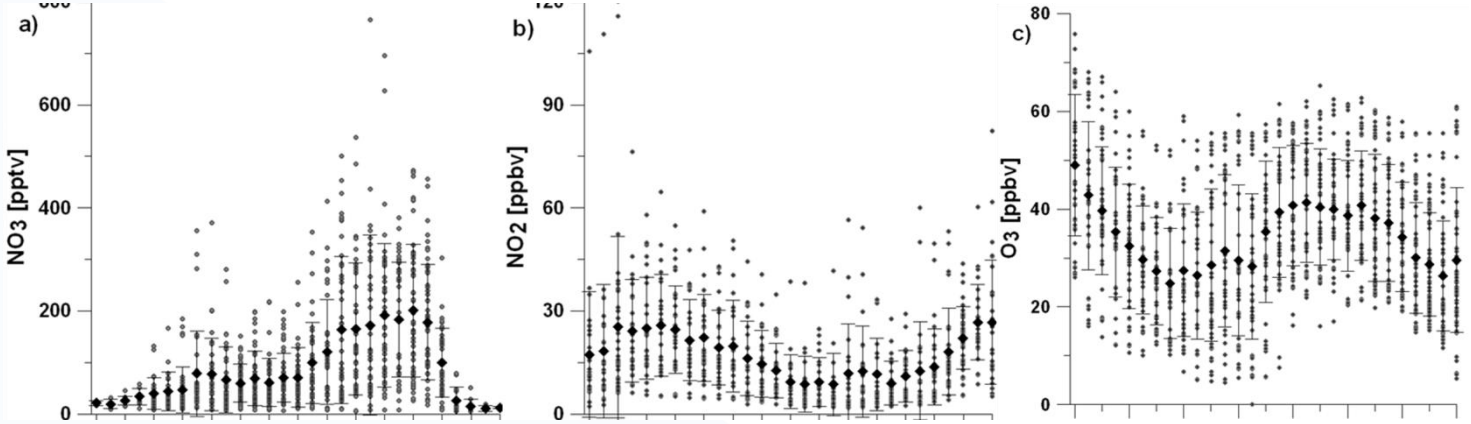
25th of July, 2007

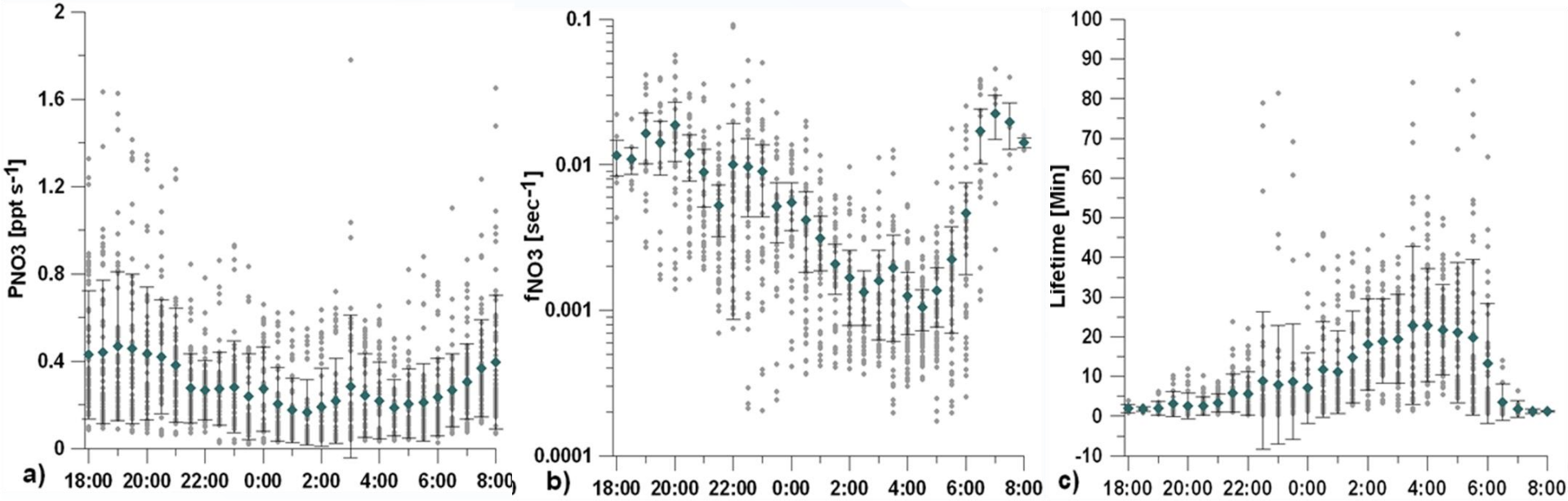


Meteorology



Half hourly mean observations of $[NO_3]$, $[NO_2]$, $[NO_3]$, P_{NO3}, f_{NO3}, τ_{NO3}



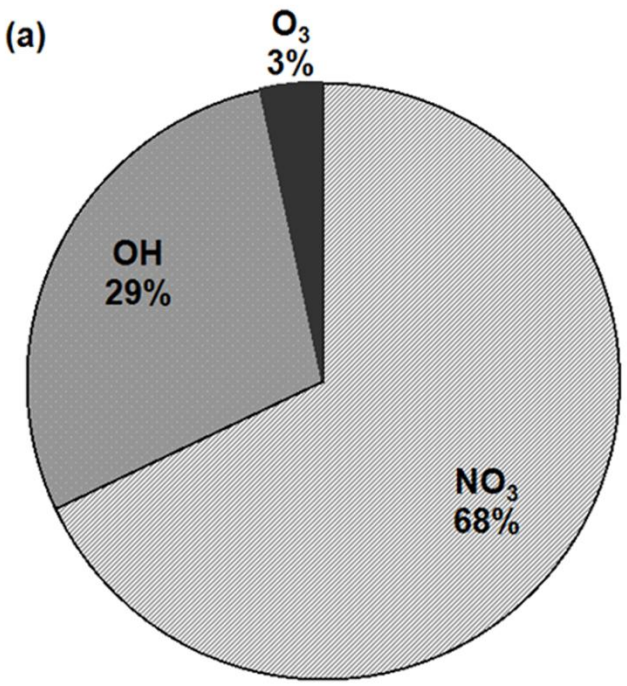


The indirect loss contributes to a lifetime k^{-1} of about 17 min, which is 1/3 of the direct loss.

NO_3 lifetimes calculated using only the degradation of NO_3 by VOCs, yielded lifetimes of ~**600** sec, similar to the average NO_3 lifetimes of ~ **750** sec calculated from the steady state assumption between 20:00 – 01:00, demonstrating the importance of

VOCs as a sink for NO_3

Comparison of the relative contribution of NO_3, OH and O_3 to the 24-hour integral of the oxidation rate at Jerusalem



$$OC = \sum_{i=1} k_{HC_i - X}[HC_i][X]$$

Data is calculated for all 30 VOCs

Comparison of the NO_3 and oxidation potential in the boundary layer

Average values	Pabstthum (Summer)	(All year)
Nighttime average maxima of NO_3, ppt	~10, peak of 70	~200, peak of 800
Maximum average of $\tau(NO_3)$, sec	~100-400	~100-1500
Relative oxidation capacity of VOCs	O_3 - 17% NO_3 - 28% OH - 55%	O_3 - 3% NO_3 - 68% OH - 29%
Relative oxidation capacity of olefinic VOCs	O_3 - 19% NO_3 - 31% OH - 50%	O_3 - 4% NO_3 - 73% OH - 23%
Reference	(Geyer et al., 2001)	This study

•Geyer, A et al., Chemistry and oxidation capacity of the nitrate radical in the continental boundary layer near Berlin *J. Geophys. Res.* **2001a**, *106*, 8013-8025.

Conclusions

Seasonality:

- Highest average and peak [NO_3] during summer & early mornings - Largest P_{NO3} and ozone intrusion during summer, accompanied by lower degradation frequencies
- Negative correlation between NO_3 & τ_{NO3} vs. RH

Losses:

- Direct loss processes of NO_3 predominate in the urban atmosphere and shorten its lifetime, especially during the warmer seasons
- Cold seasons are dominated by indirect N_2O_5 losses

Extreme elevated [NO_3] are consequence of:

- Increase in [O_3]; [NO_2]; τ_{NO3}~25min
- Decrease in RH; [NO]; f_{NO3}

- NO_3 is a dominant oxidant under urban conditions

Acknowledgments

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