

Large Day-Time Source of Nitrous Acid (HONO)

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- The OH radical is a key species in atmospheric chemistry:
 - OH chemistry controls the removal rate of most air pollutants
 - OH chemistry leads to the formation of ozone

- Main sources of OH:
 - O₃ photolysis
 - HCHO photolysis
 - VOC's + O₃
 - HONO photolysis

- Known/measured sources and sinks of OH are often not balanced
e.g.: “unknown OH-reactivity” (*Di Carlo et al., 2004*)

- Since the first unequivocal detection (*Perner&Platt, 1979*) nitrous acid (HONO) is known to be a major OH source in the morning (e.g. *Alicke et al., 2003*):



- However, during the day HONO was almost always below the detection limit in old studies, in good agreement with the *photo-stationary state* (PSS) of known sources and sinks (only few pptv!), including the measured night-time sources
- Nevertheless, using the measured HONO in the morning and the theoretical HONO during daytime, an integrated HONO contribution to the OH formation of up to **34 %** was estimated! (*Alicke et al., 2002*)

- In recent studies with instruments with improved detection limit, HONO levels well above the PSS were observed:

- Switzerland	rural: 50-100 pptv	(Nefstel et al., 1996)
- Wuppertal	urban: 50-150 pptv	(Kleffmann et al., 2002)
- New York state	rural: ~ 50 pptv	(Zhou et al., 2002)
- Karlsruhe	urban: 150-200 pptv	(Kleffmann et al., 2003)
- New York	urban: 400-500 pptv	(Ren et al., 2003)

- ➔ In these studies a strong daytime source of HONO was postulated
- ☹ However, the PSS was never completely constrained by measured parameters in these studies, i.e.: [OH], [NO_x], [HONO], J(HONO)
- 💣 In addition, wet chemical instruments were used in all these studies, which might suffer from interferences...

→ Aim of the study:

- First simultaneous daytime measurements of HONO, NO_x, OH and J(HONO)
- Sensitive HONO measurements with a validated instrument
- ➔ Quantification of the daytime source of HONO completely by measured parameters
- Additional measurements of O₃, HCHO, VOC's, J(O¹D), J(HCHO)
- ➔ Relative contribution of the different OH radical sources



Measurement site:

On a tower in 38 m altitude in a forest on the Forschungszentrum Jülich, during the ECHO 2003 campaign

“Semi-urban” (10-20 ppbv NO_x in the morning...)

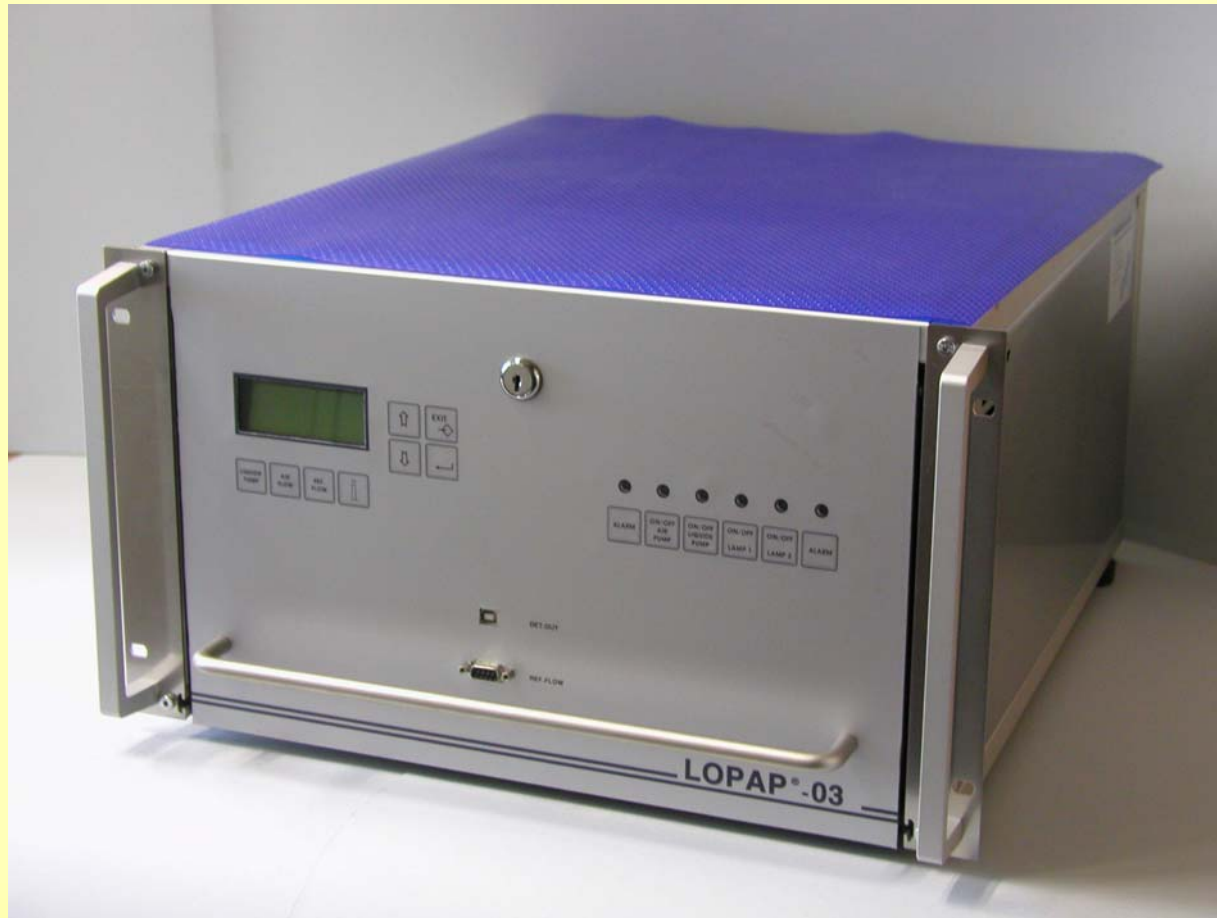
HONO, OH and radiation measured in-situ on the tower

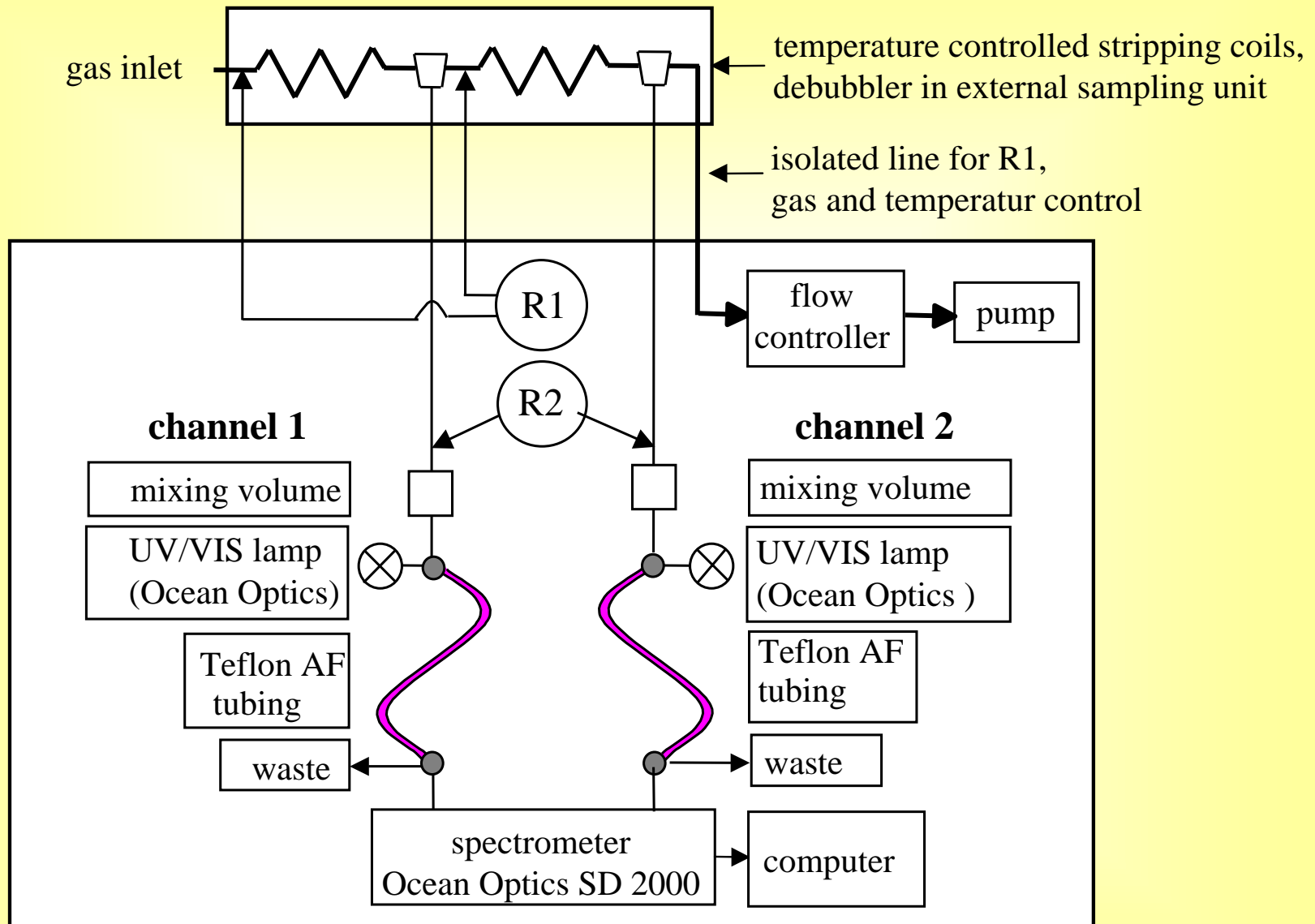
NO_x , O_3 , HCHO, VOC's measured at the bottom of the tower (sampling lines)

Instrumentation:

- OH/HO₂:** Laser-induced fluorescence (LIF) instrument:
DL = $5 \times 10^5 \text{ cm}^{-3}$, 90 s time resolution
- NO and NO₂:** Chemiluminescence analyzer (ECO PHYSICS TR480) with photolytic converter (ECO PHYSICS PLC760): DL = 5 and 10 pptv, 60 s time resolution
- HCHO:** Hantzsch instrument (Aero Laser AL 4001):
DL = 30 pptv, 3.5 min time resolution
- O₃:** UV absorption spectrometer (ANSYCO O341M):
DL = 0.5 ppbv, 60 s time resolution
- VOC's:** GC-FID, thermal desorption and a cryo focus modul
- J-values:** Scanning spectroradiometer, filter radiometers:
J(O¹D), J(NO₂)

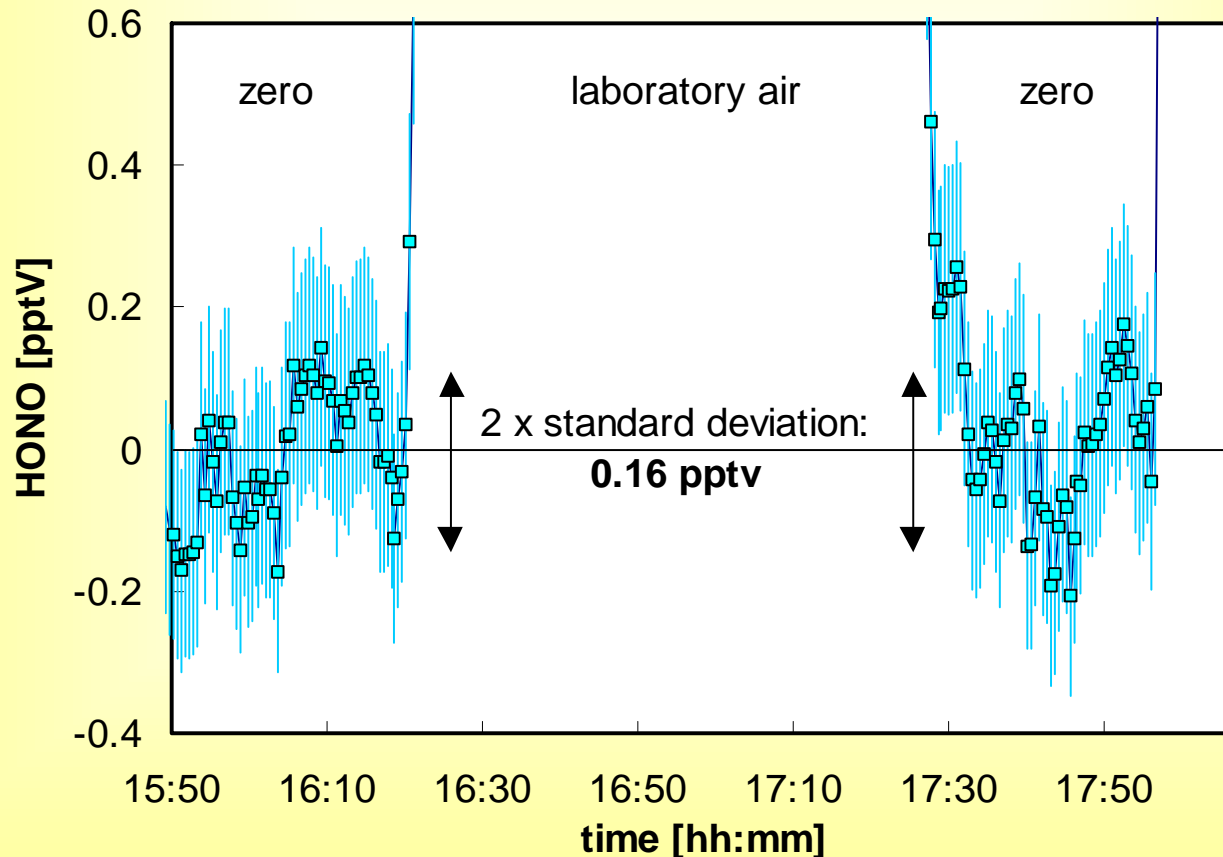
HONO: long path absorption photometer (LOPAP)





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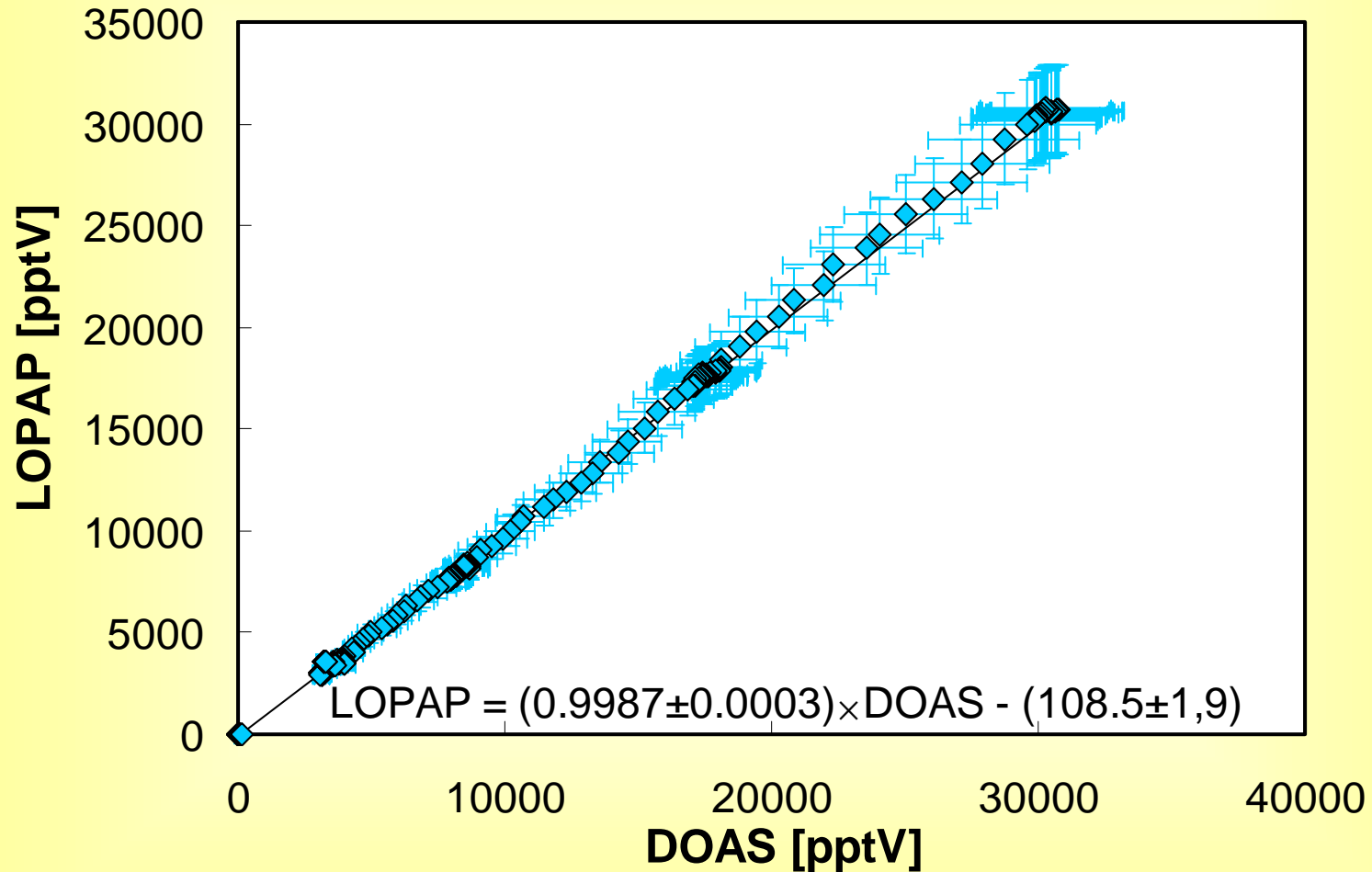
- DL = 1-2 pptv (this study), recently improved to 0.2 pptv
- Time resolution: 2-7 min (10-90 % signal), this study 4 min



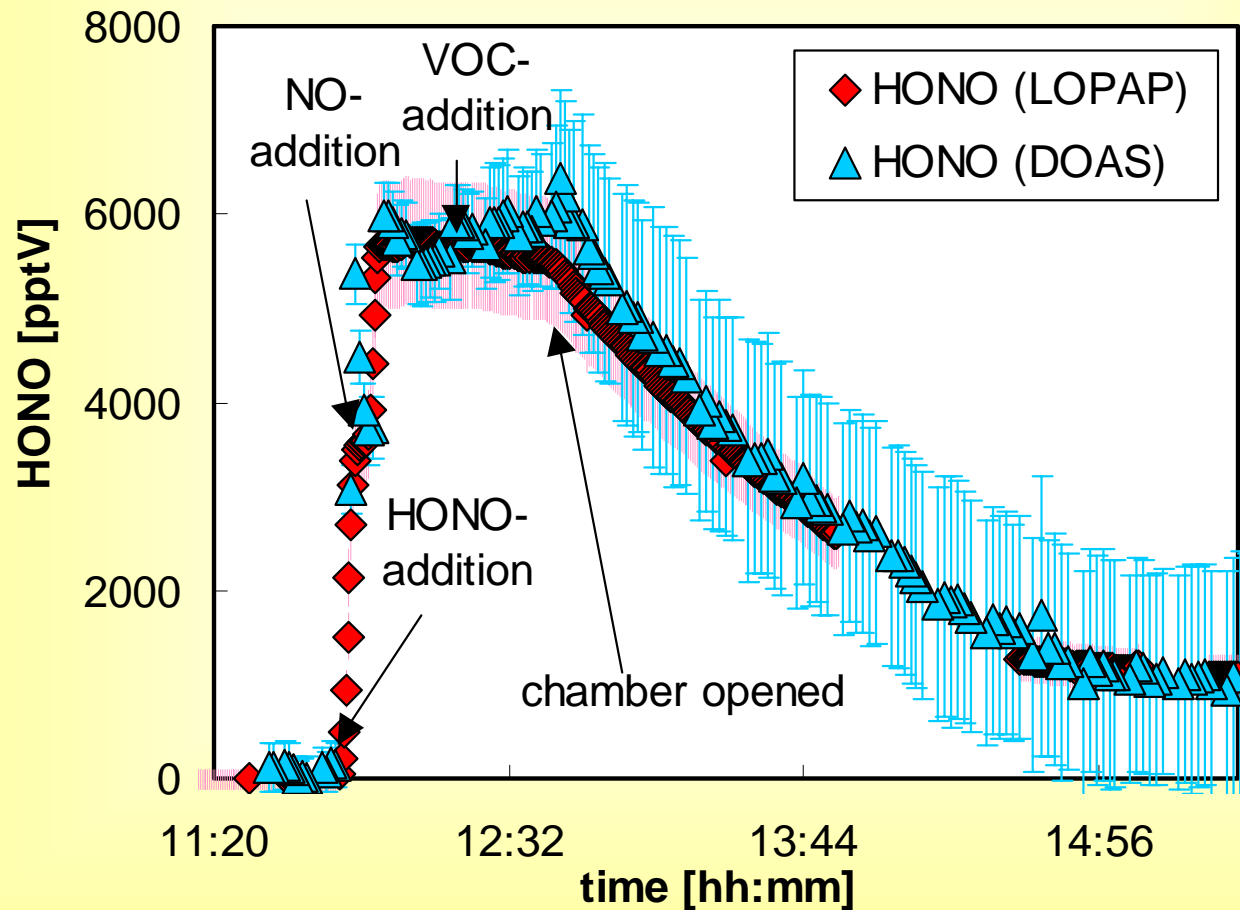
HONO: long path absorption photometer (LOPAP)

- Instrument validated against the DOAS technique:
- ➔ Excellent agreement in the field and in a smog chamber also for daytime measurements/photolysis experiments

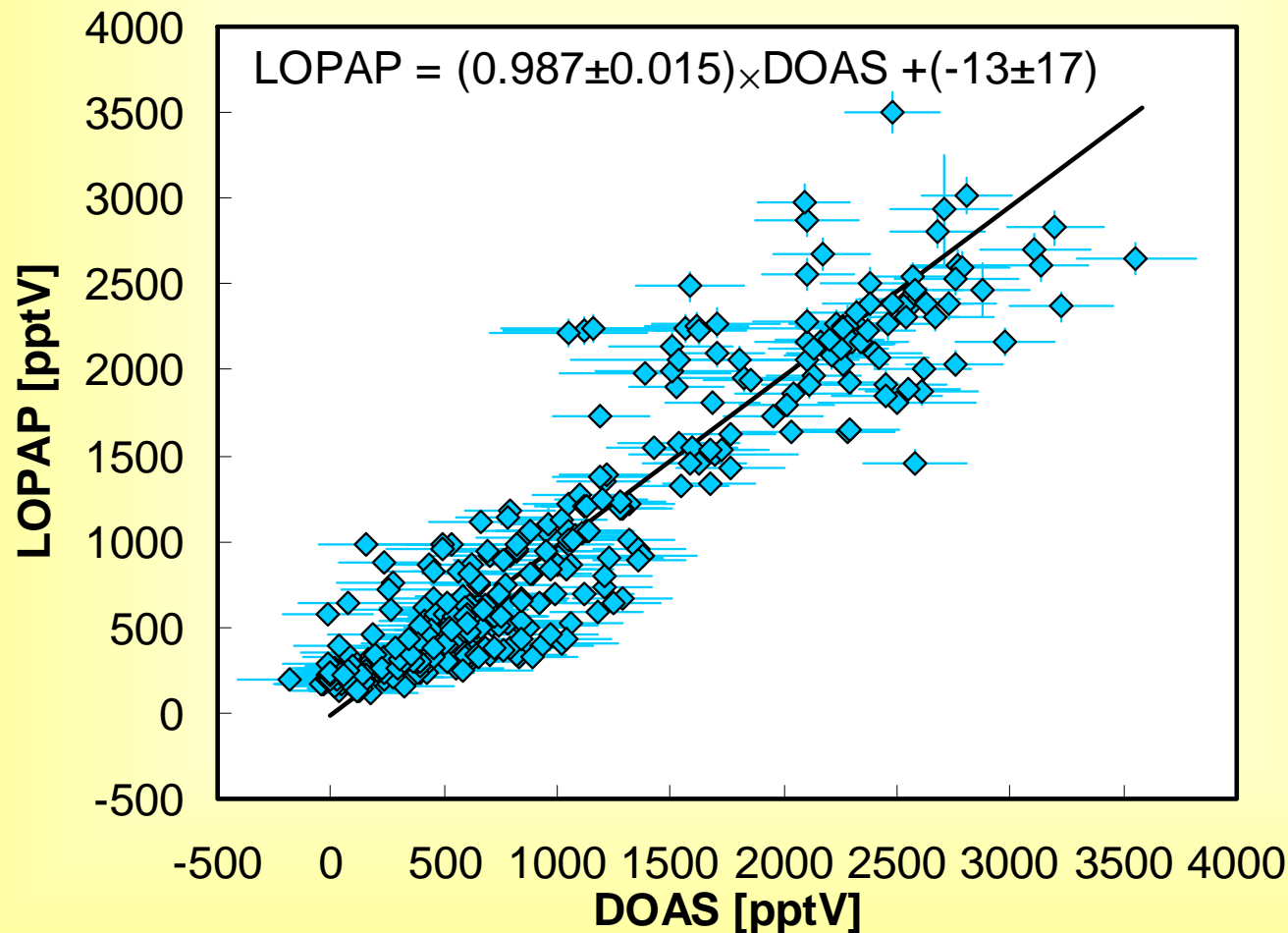
○ Pure HONO/NO_x mixture in a smog chamber in the dark



- Photosmog experiment in a smog chamber (200 ppbv NO_x , 150 ppbv toluene, 450 ppbv ethene, 450 ppbv n-butane + hv)



- Field measurement in Milan (FORMAT) using an open White mirror system for the DOAS (→ same air mass)



HONO: long path absorption photometer (LOPAP)

➔ LOPAP instrument measures daytime concentrations correctly

💣 In all other intercomparisons between chemical instruments and the DOAS technique higher concentrations were observed during the day by the chemical detectors:

Appel et al., 1990

Febo et al., 1996

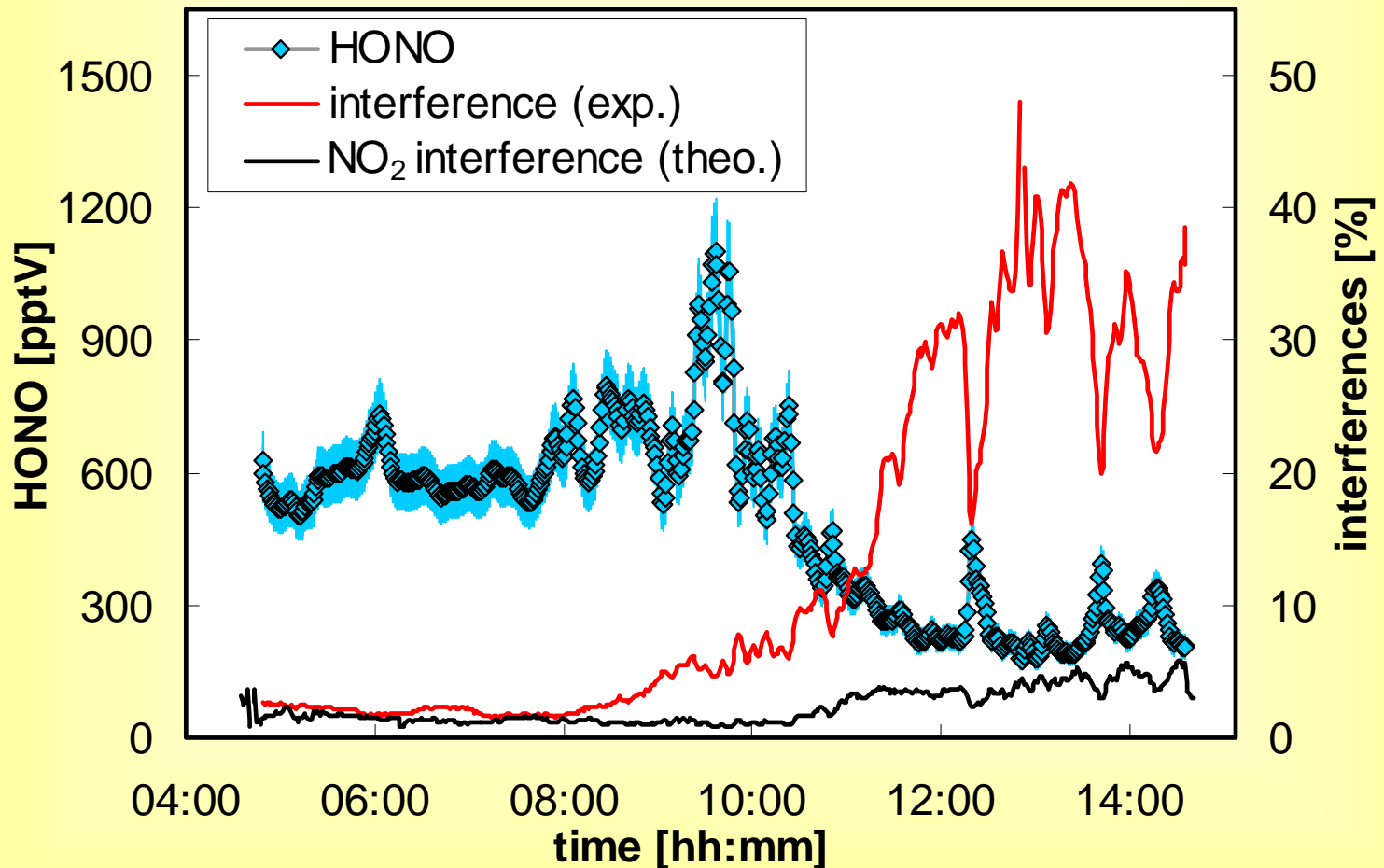
Coe et al., 1997

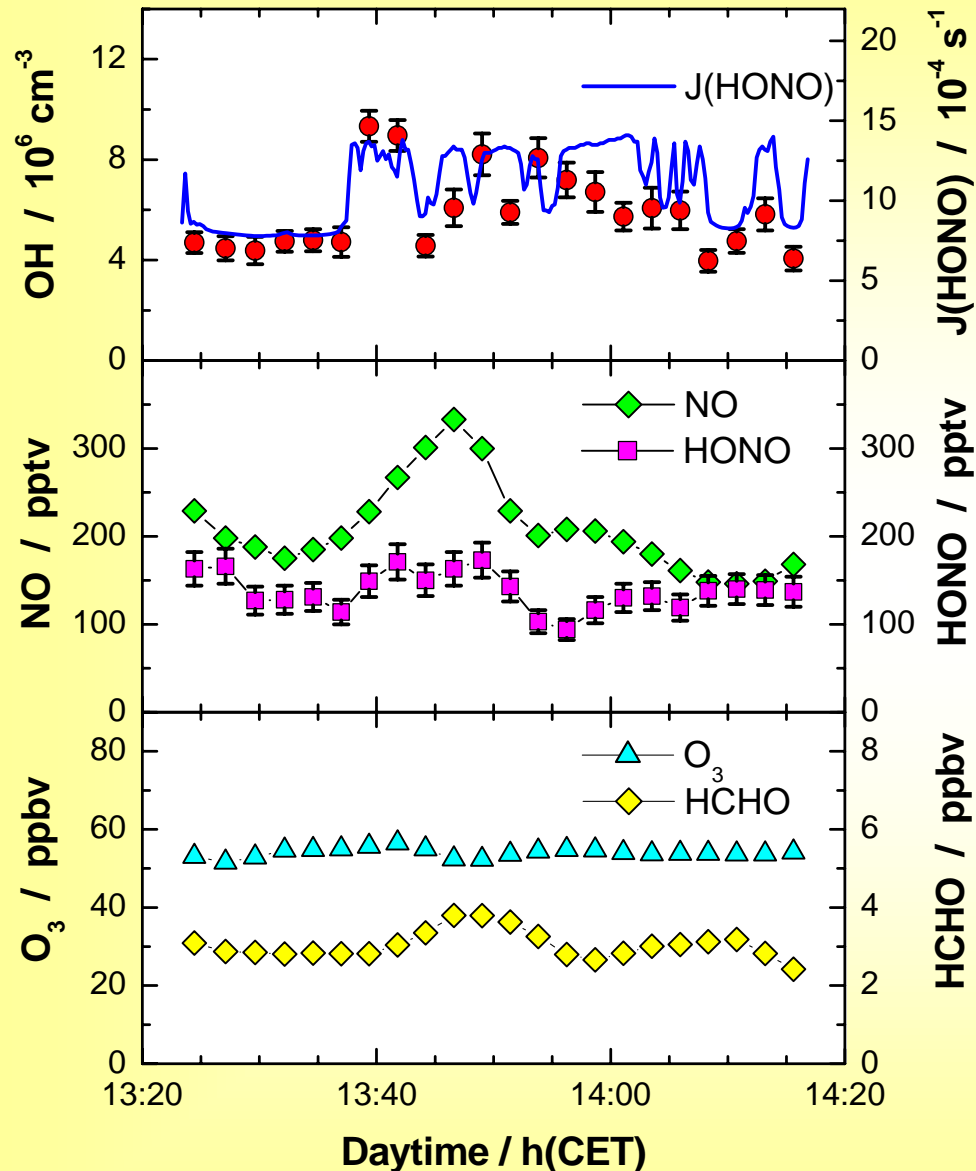
Müller et al., 1999

➔ Interferences of the chemical detectors...

↔ Interferences are corrected for by the LOPAP instrument

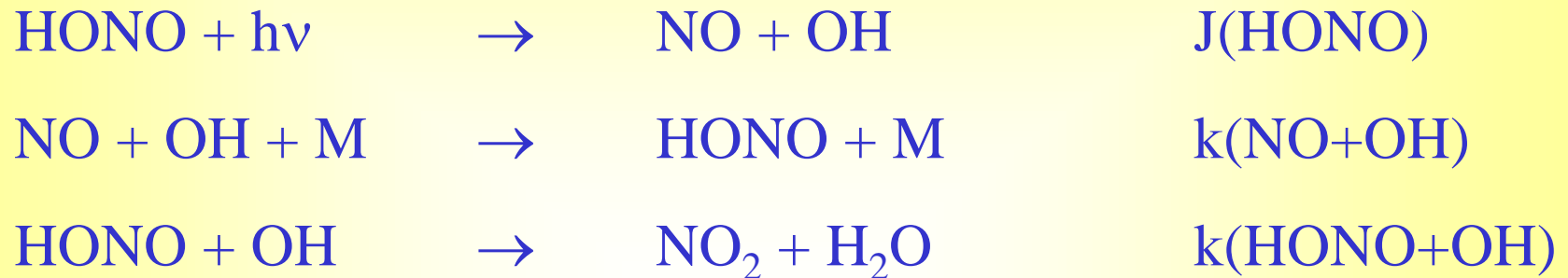
- Correction of interferences (2 channel system) very important for daytime measurements (→ unknown interferences!)





Example of the results:

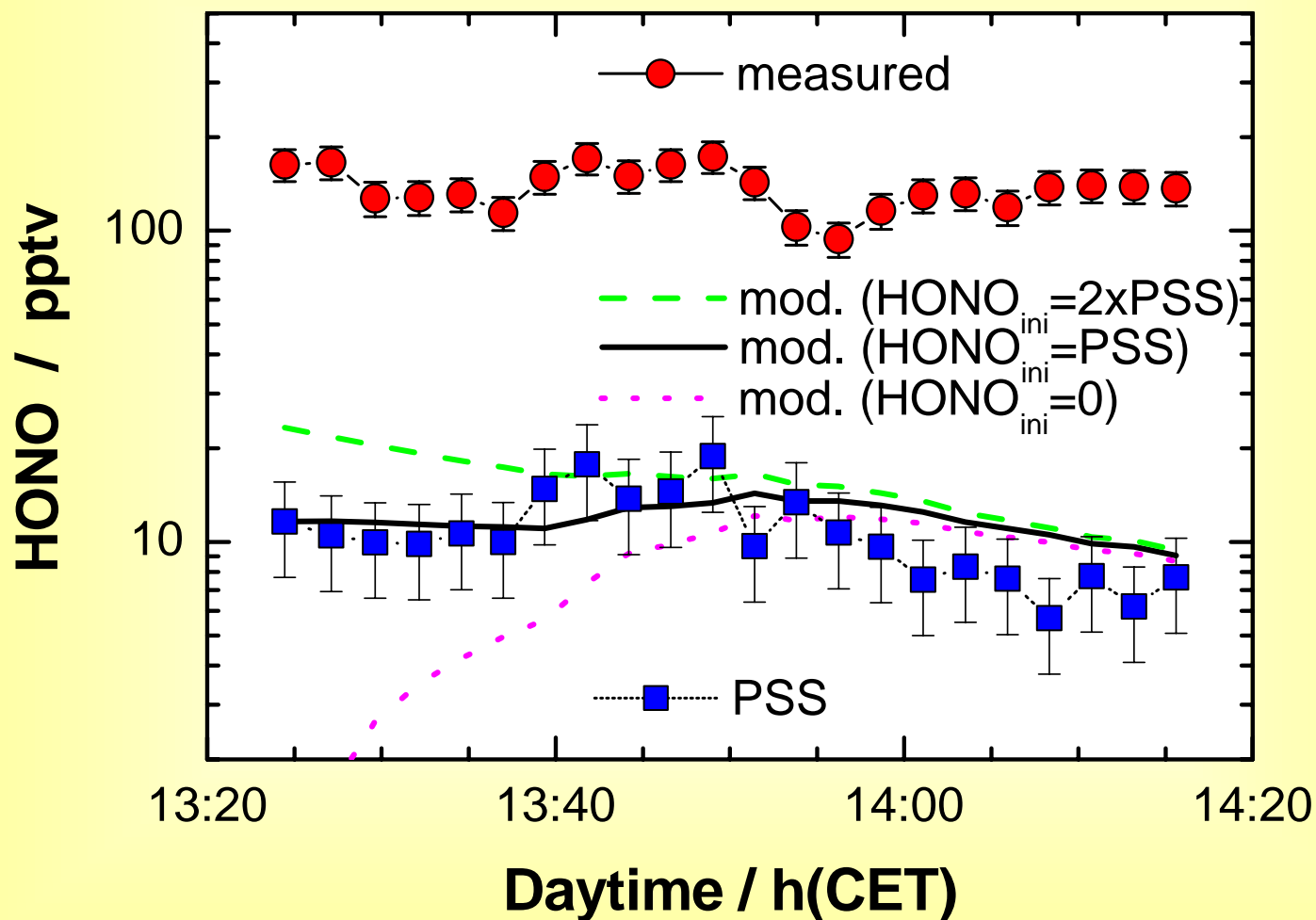
- 1 hour period around noon on the 29.07.03
- Sunny with some thin clouds
- High [HONO] \approx 140 pptv (typical for the campaign)
- Low [NO]
- ➔ Low [HONO]_{PSS}

PSS of HONO (only gas phase chemistry):

$$[\text{HONO}]_{\text{PSS}} = \frac{k_{(\text{NO}+\text{OH})} \times [\text{NO}] \times [\text{OH}]}{J_{(\text{HONO})} + k_{(\text{HONO}+\text{OH})} \times [\text{OH}]}$$

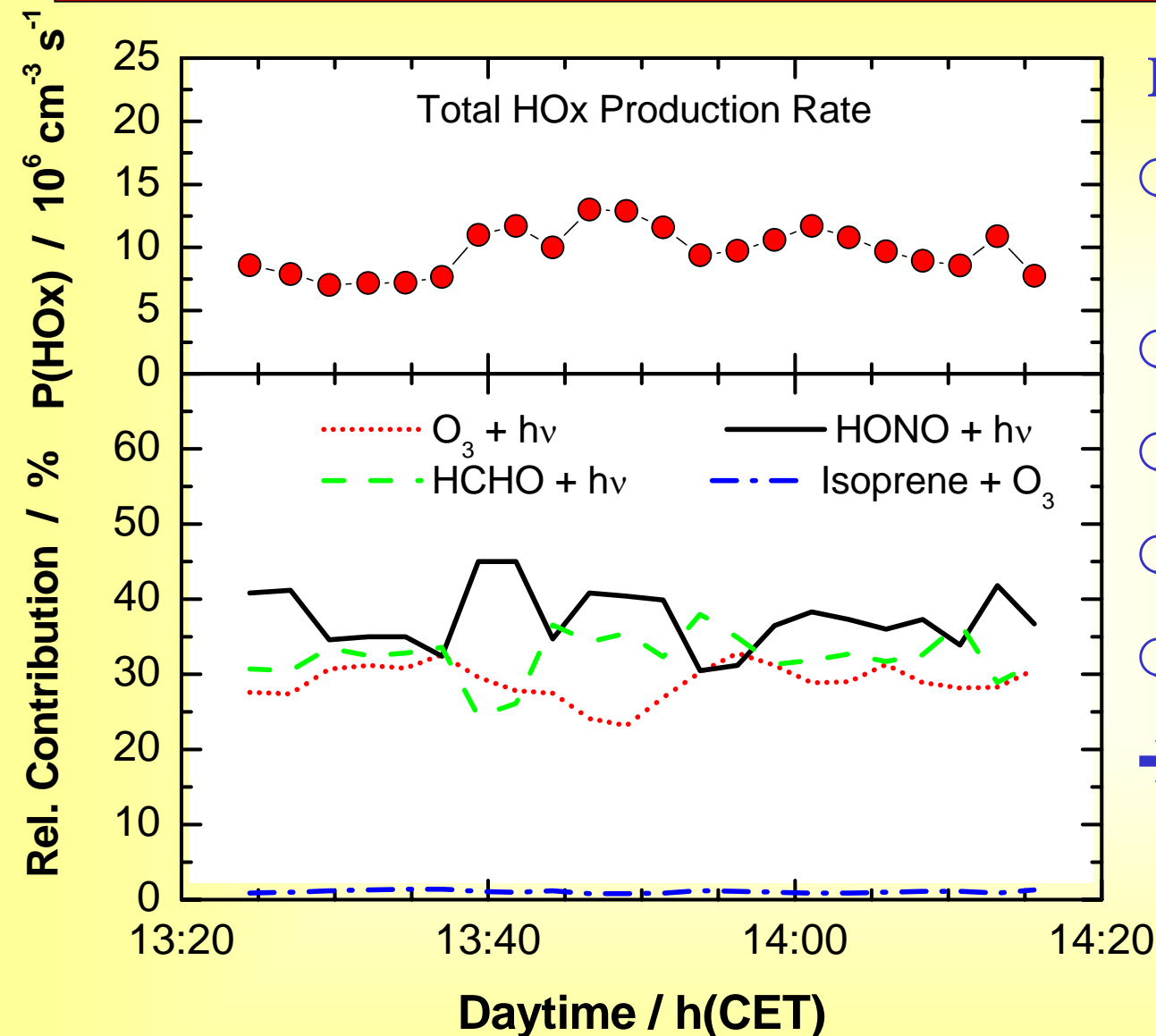
Recommended values (IUPAC) for the rate constants were used

→ mean $[HONO]_{PSS}$ of ~ 11 pptv (\ll measured!)



- Additional HONO source of ~ **500 pptv/h** necessary!
- ➔ Emissions and heterogeneous formation by NO₂ on the ground?
(Can explain night-time formation, see *Vogel et al.*, 2003)
- From the measured increase of the HONO/NO_x ratio during the following night ➔ $k(\text{het+em})$ of $1.2 \times 10^{-6} \text{ s}^{-1}$
- ➔ Around noon only **8 pptv/h** can be explained by emissions and heterogeneous formation on the ground
- ➔ Daytime source is ~**60 times larger** than the night-time source!
- Source strength is in good agreement with recent studies

<i>Kleffmann et al.</i> , 2002, 2003:	day 20 × night (urban)
<i>Ren et al.</i> , 2003:	1800 pptv/h (urban)
<i>Zhou et al.</i> , 2002:	200 pptv/h (rural)

**Relative contribution:**

○ Total HO_x production: $\sim 10^7 \text{ cm}^{-3} \text{ s}^{-1}$

○ HONO: 35 %

○ HCHO: 30 %

○ O₃: 27 %

○ VOC's+O₃: 8 %

➔ HONO most important OH source around noon!!

- First simultaneous quantification of HONO, OH, NO_x and radiation
- PSS of HONO completely constrained by measured parameters
- High HONO concentrations during daytime: **13 × [HONO]_{PSS}**
- ➔ Daytime source of HONO of **500 pptv/h**, ~ **60 ×** nighttime source!
- ➔ HONO is the most important OH source at the measurement site during the day
- ➔ Most probably a global source, elevated HONO observed: Arctic, Zugspitze, rural and urban influenced forest, urban: Wuppertal, Karlsruhe, New York...)

- ☞ Mechanism of the daytime source should be identified!
(photolysis of adsorbed nitrate/ HNO_3 was postulated, but...)
- ☞ HONO should be measured in addition to O_3 and HCHO in field campaigns
- ☞ Known sources of HONO (emission & heterogeneous formation on surfaces) should be included in models
- ☞ Daytime source should be included in models

Acknowledgements

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**Thank you for your
attention!**