

Measurements of HONO during OASIS in Barrow, Alaska

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- Nitrous Acid (HONO) direct OH source:
$$\text{HONO} + h\nu (<390 \text{ nm}) \rightarrow \text{NO} + \text{OH}$$
- OH: "cleaning detergent of the atmosphere"
- For polar conditions HONO was proposed to be one of the most important OH sources
- Different heterogeneous formation mechanisms proposed:
$$\text{NO}_3^- + h\nu \rightarrow \text{NO}_2^- (\rightarrow \text{HONO}) + \text{O}$$
$$2 \text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{HNO}_3$$
$$\text{NO}_2 + \text{humic acid} + h\nu \rightarrow \text{HONO} + \text{products}$$
- Still under discussion...

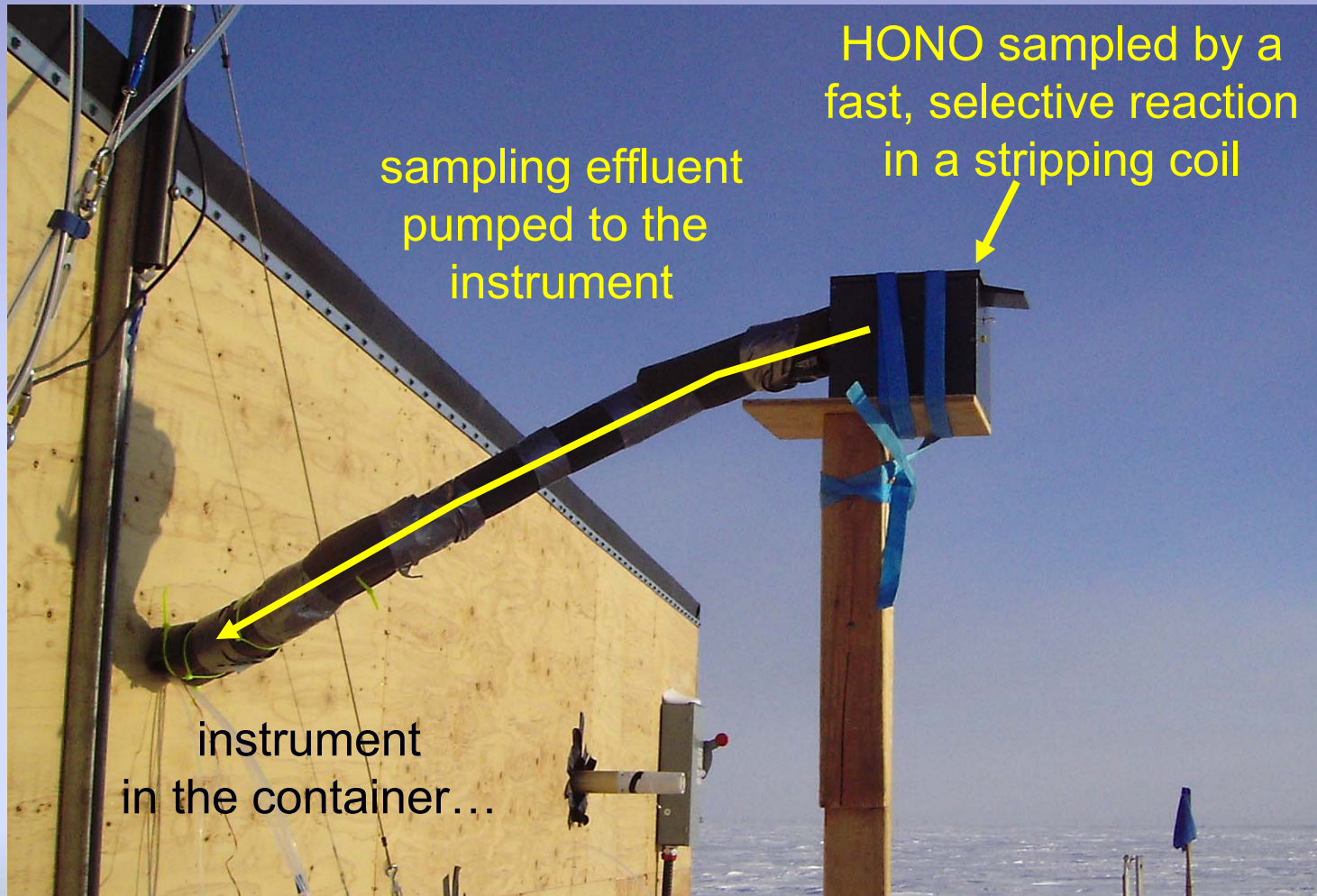
- Polar HONO was mostly measured by "wet chemical" instruments (mistchambers, denuders, coil/HPLC...)
- 💣 The only polar HONO intercomparison show a **factor of 7** overestimation of a mist-chamber/IC compared to the spectroscopic LIF technique (*Liao et al., 2006*)
- 💣 Models indicate strong overestimation of measured polar HONO levels (*e.g. Bloss et al., 2006*)
- ➔ "Wet chemical" HONO measurements may be affected by strong interferences
- Still under discussion...

- Interference-free measurement of HONO in polar regions during OASIS in Barrow, Alaska
- Has [HONO] been overestimated before?
- Is HONO a net source of OH radicals in polar regions?
- What is the formation mechanism of HONO in polar regions?

- HONO was measured by the LOPAP instrument
- interferences are corrected
- no sampling lines
- validated (DOAS)
- extremely sensitive:
DL: 0.2 pptV

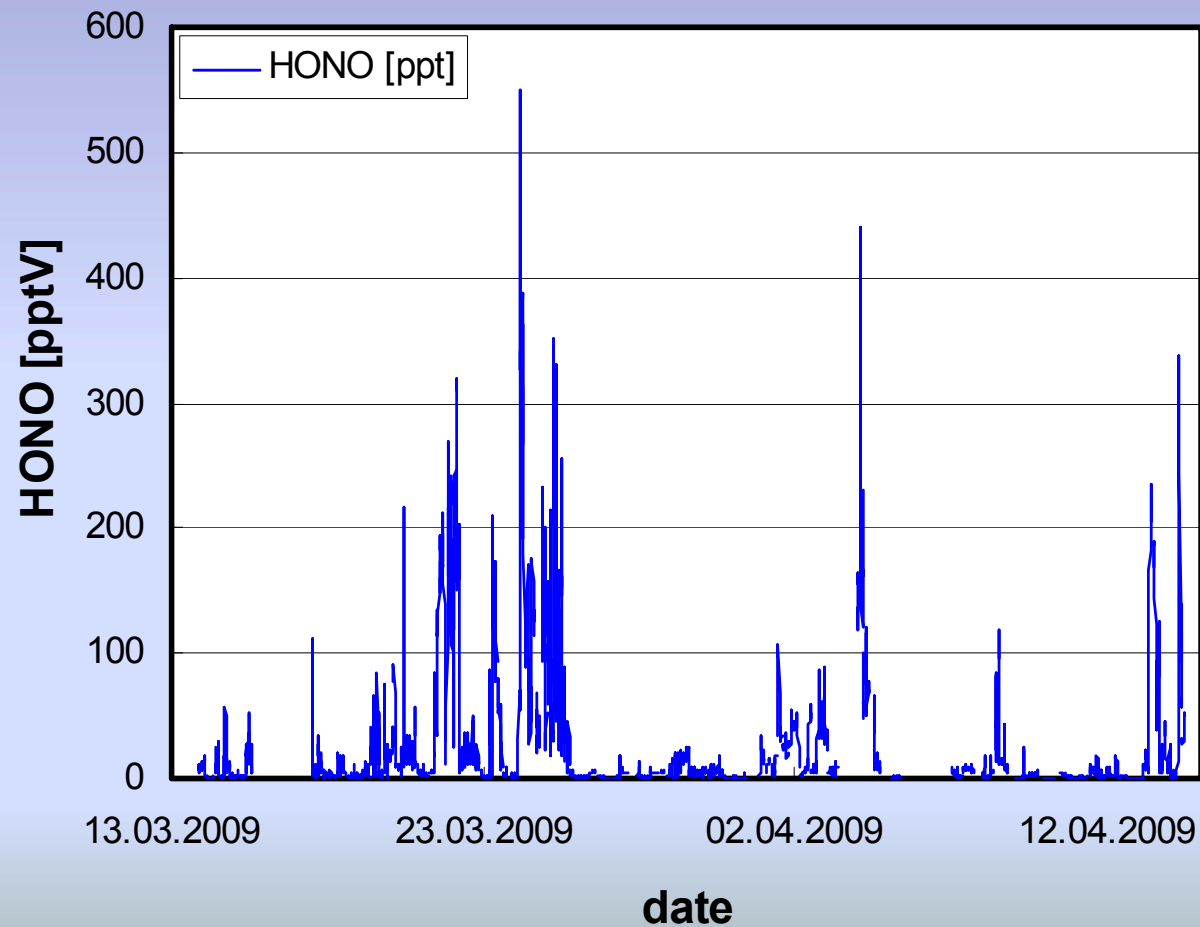


- External sampling unit → no sampling lines

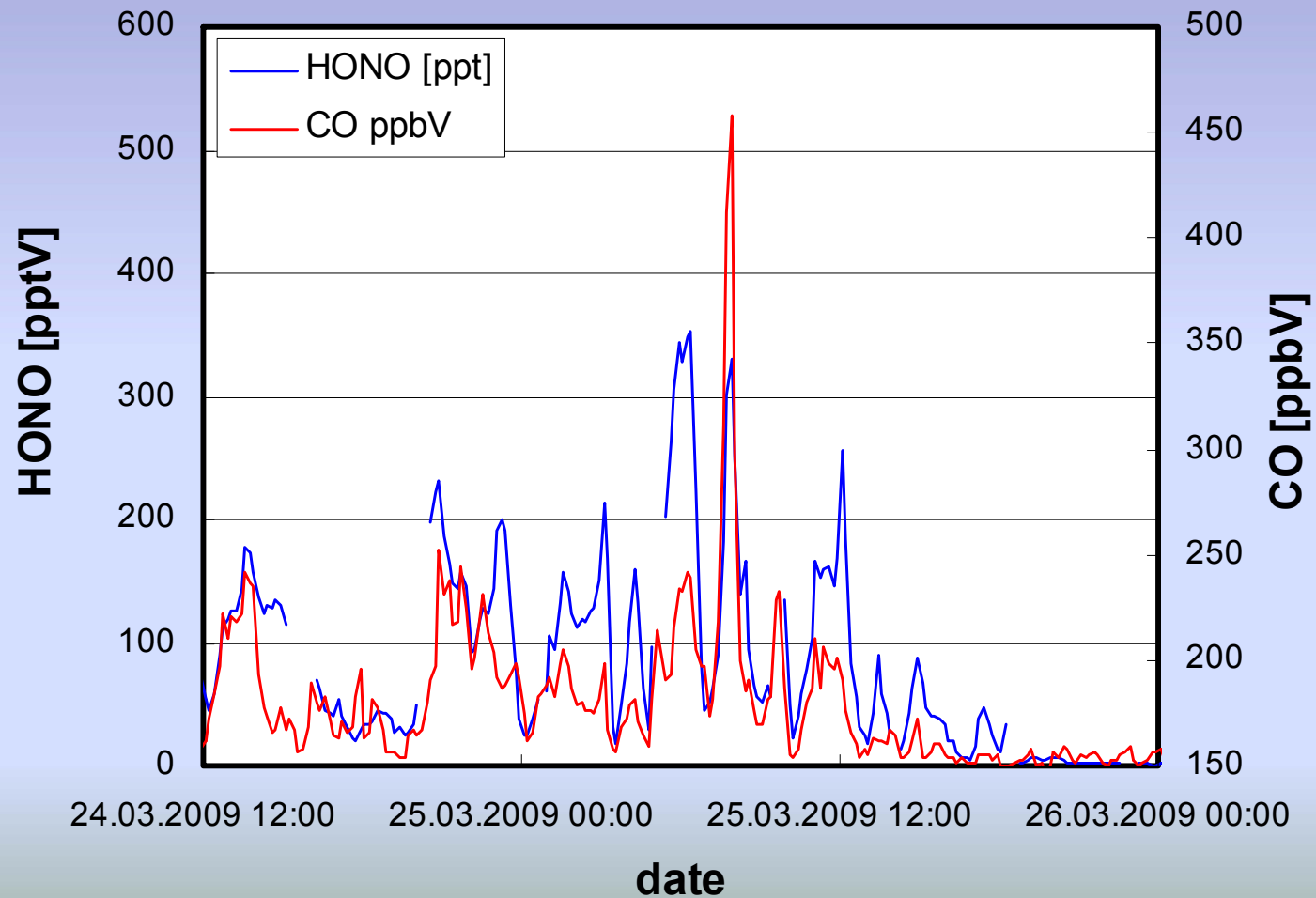


- Other parameters used for evaluation:
 - OH (NCAR)
 - NO, NO₂, NO_y (NCAR)
 - J-values (NCAR)
 - O₃ (NCAR)
 - meteorological data (Environment Canada)

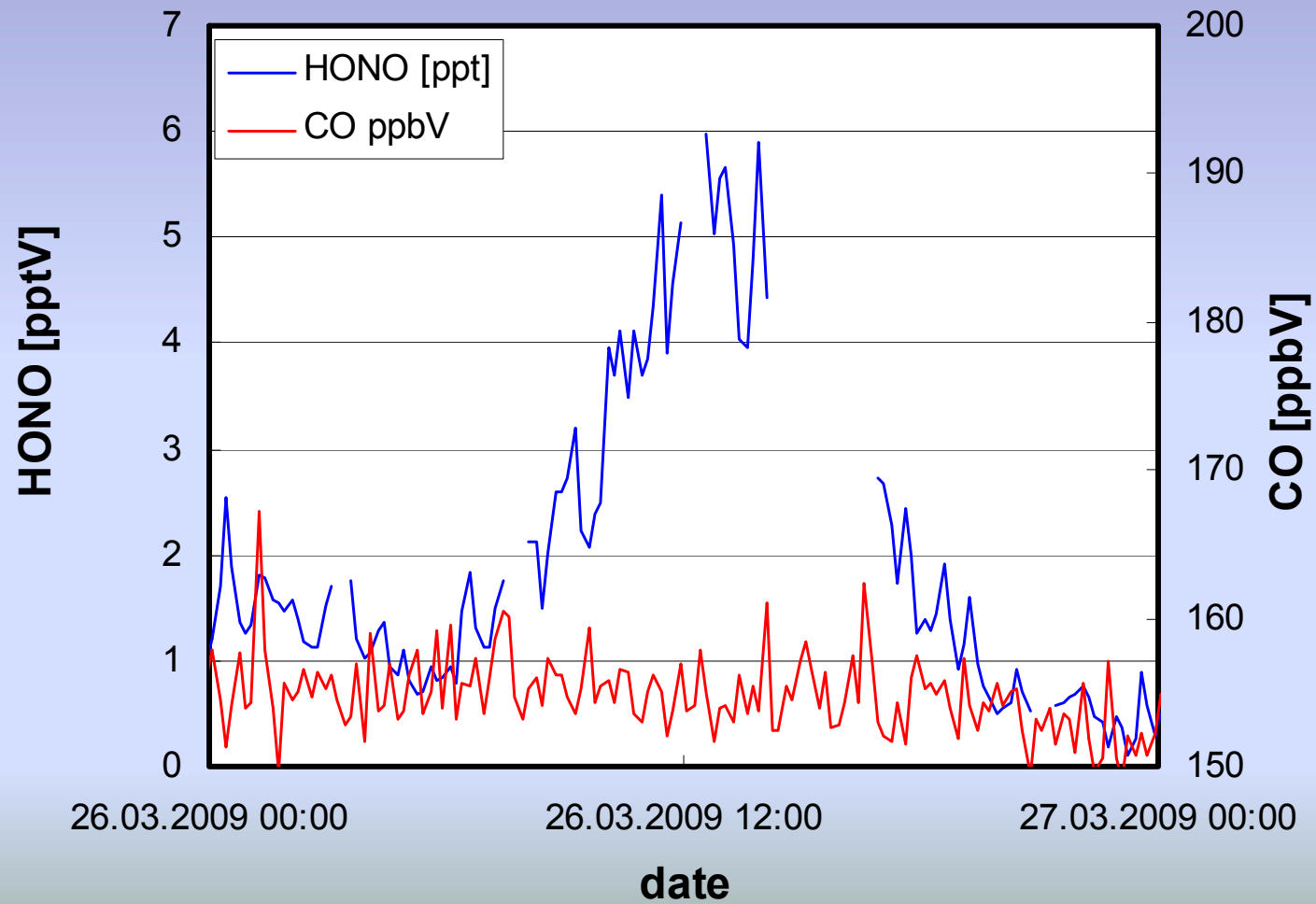
- HONO was measured from 13th March - 14th April
- Very high concentrations often observed



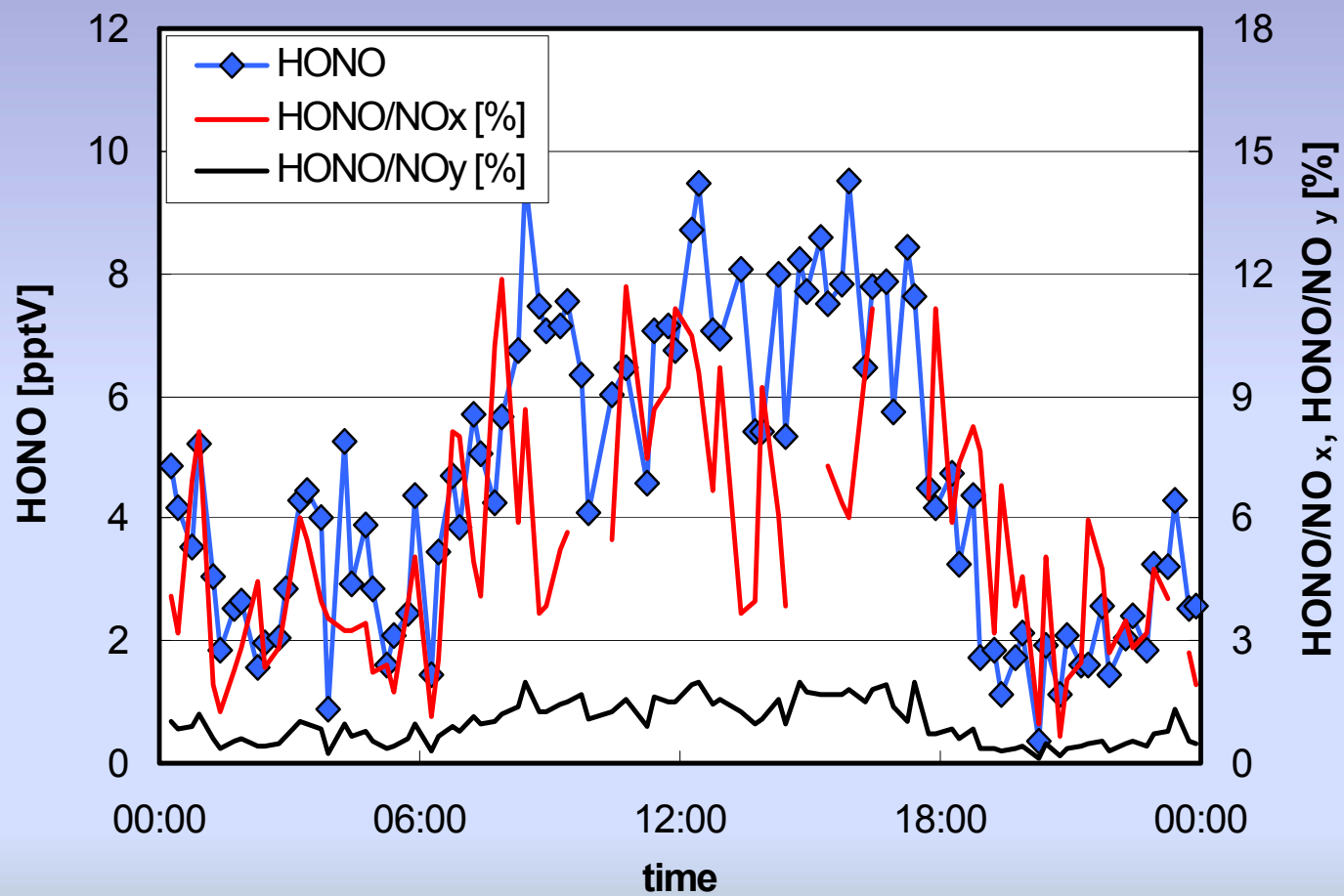
- High correlation with CO
- ➔ Local emissions from BARC and Barrow...



→ Only "clean" days considered



- "Average" clean day



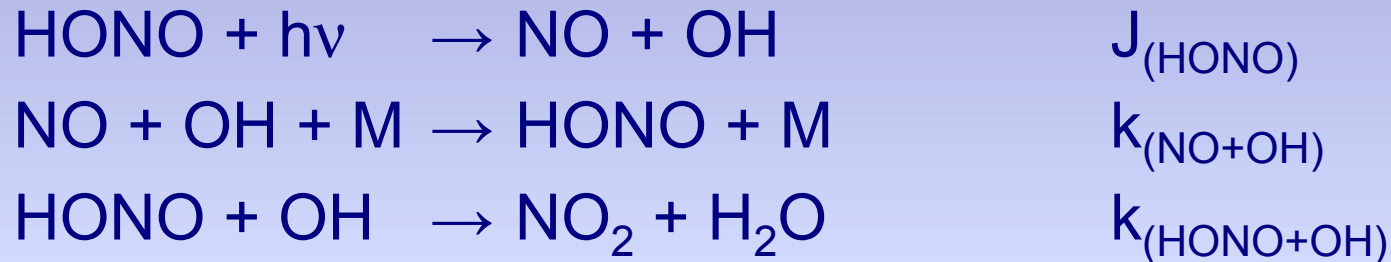
- **OASIS average clean day:**
 - $\text{HONO/NO}_x = 5.3 \pm 2.8 \%$
 - $\text{HONO/NO}_y = 1.0 \pm 0.5 \%$

- **In excellent agreement with other remote LOPAP data:**
 - *Zugspitze*: $\text{HONO/NO}_x = 2.5 \%$, $\text{HONO/NO}_y = 1.0 \%$
 - *Jungfraujoch*: $\text{HONO/NO}_x = 4.6 \%$, $\text{HONO/NO}_y = 1.1 \%$

- **Factor ≥ 4 lower compared to most other polar data**
 - $\text{HONO/NO}_x = 20\text{-}100 \%$

- Was explained by interferences (*Kleffmann and Wiesen, 2008*)
- ➔ Should be corrected for also for other instruments

- Theoretical HONO daytime level by photostationary state (PSS) assumption and known gas phase reactions:

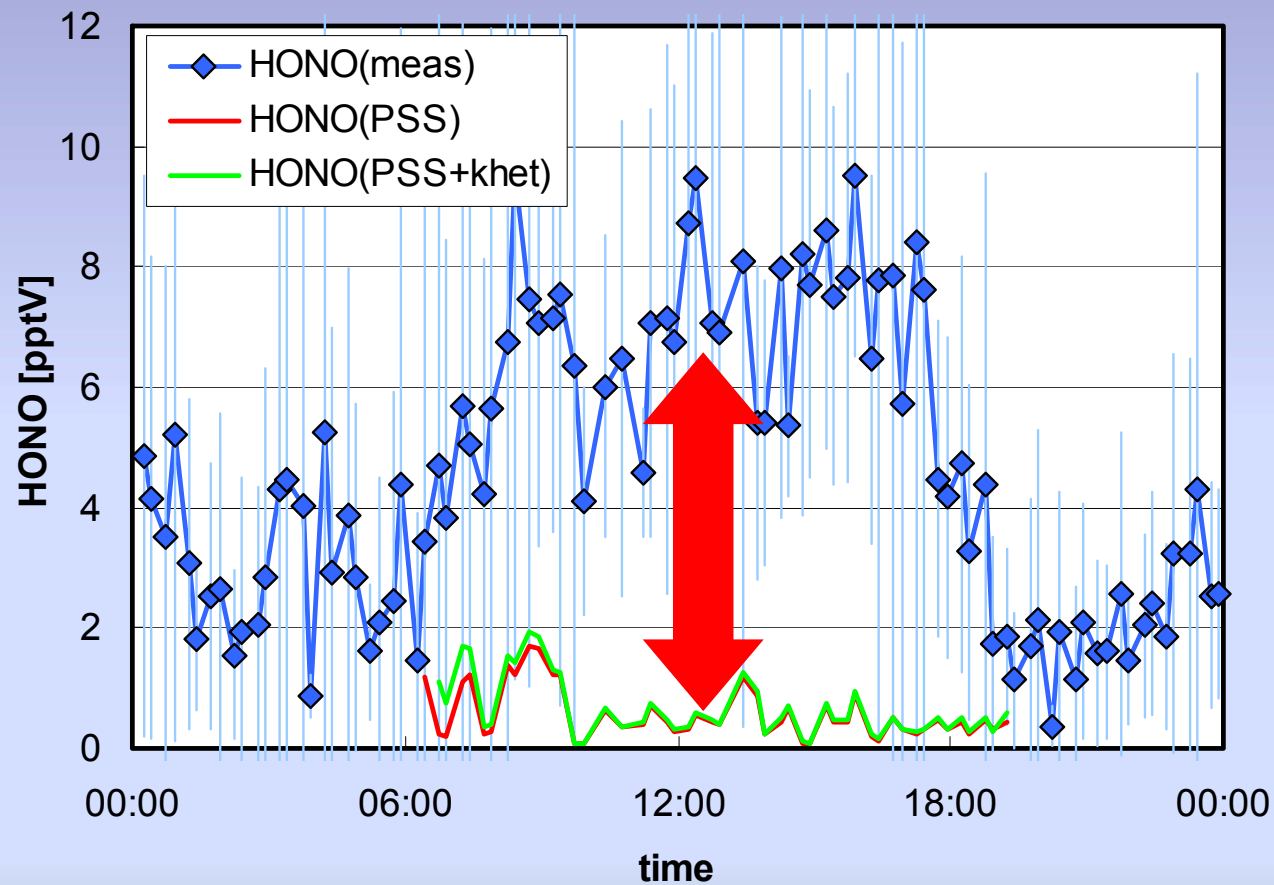


$$[\text{HONO}]_{\text{PSS}} = \frac{k_{(\text{NO}+\text{OH})} \times [\text{NO}] \times [\text{OH}]}{J_{(\text{HONO})} + k_{(\text{HONO}+\text{OH})} \times [\text{OH}]}$$

known (IUPAC) measured

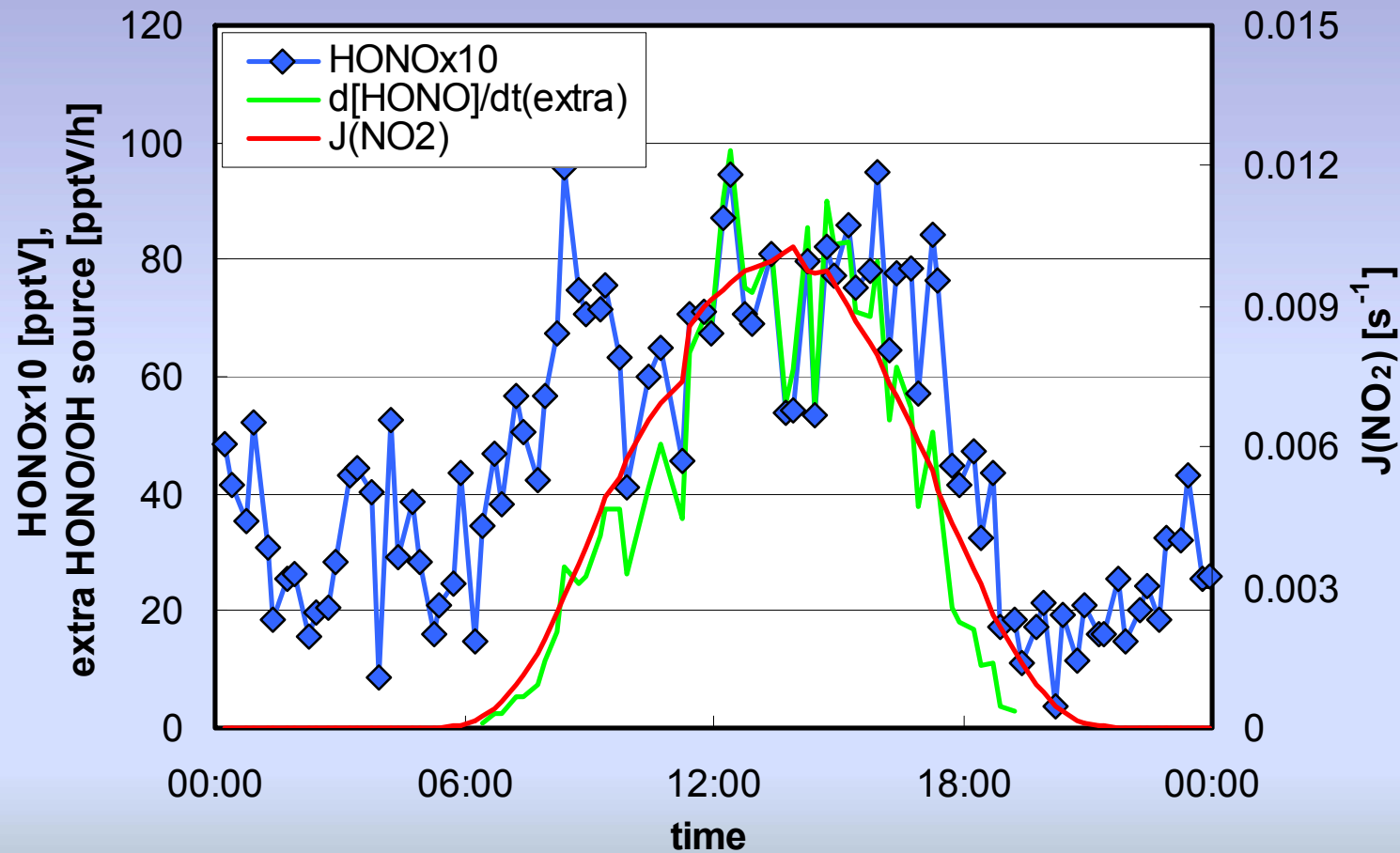
→ $[\text{HONO}]_{\text{theo.}}$ can be calculated during daytime

○ $[\text{HONO}]_{\text{meas.}} \gg [\text{HONO}]_{\text{theo.}}$

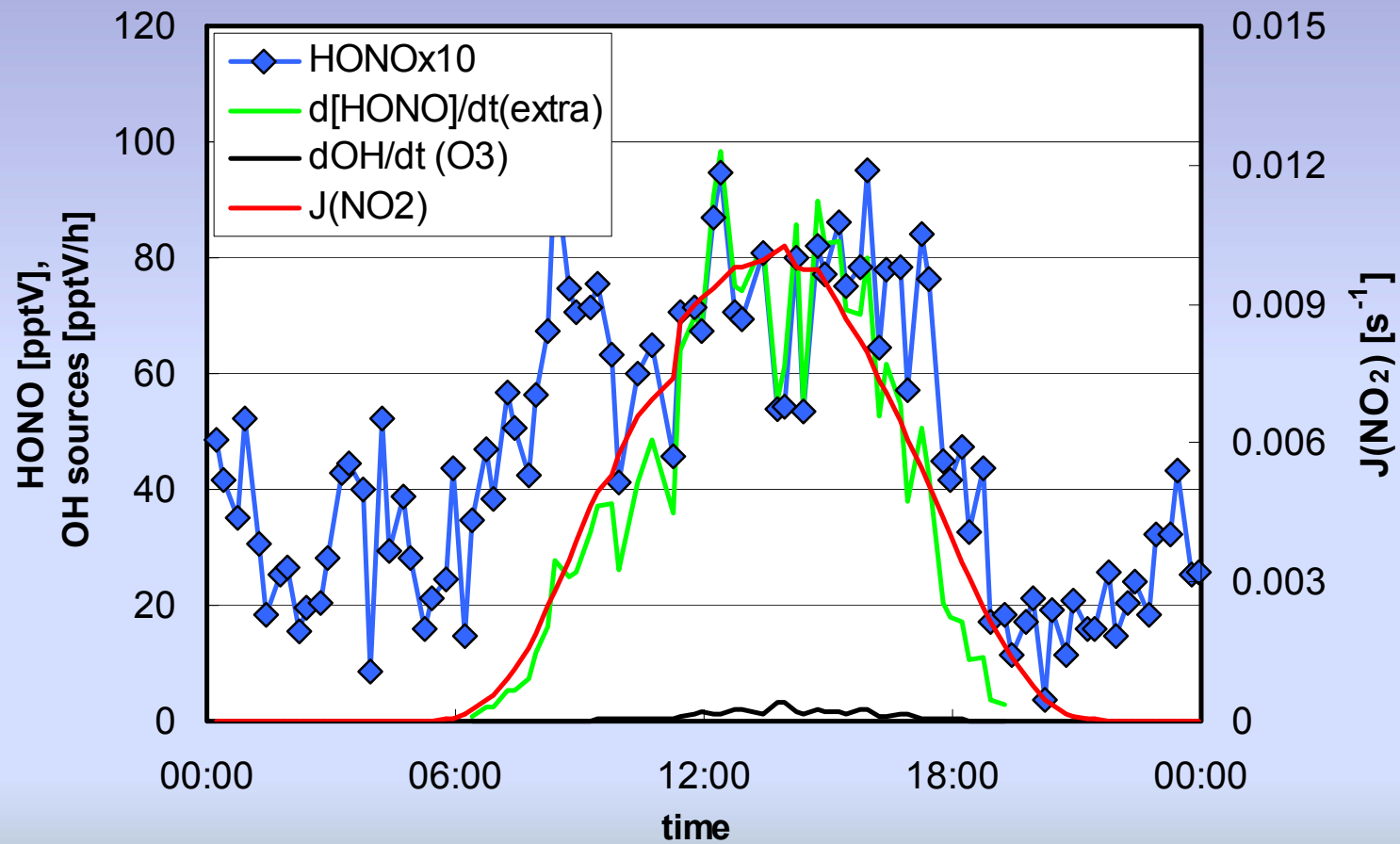


Extra HONO/OH source: $d[\text{HONO}]/dt_{\text{extra}}$

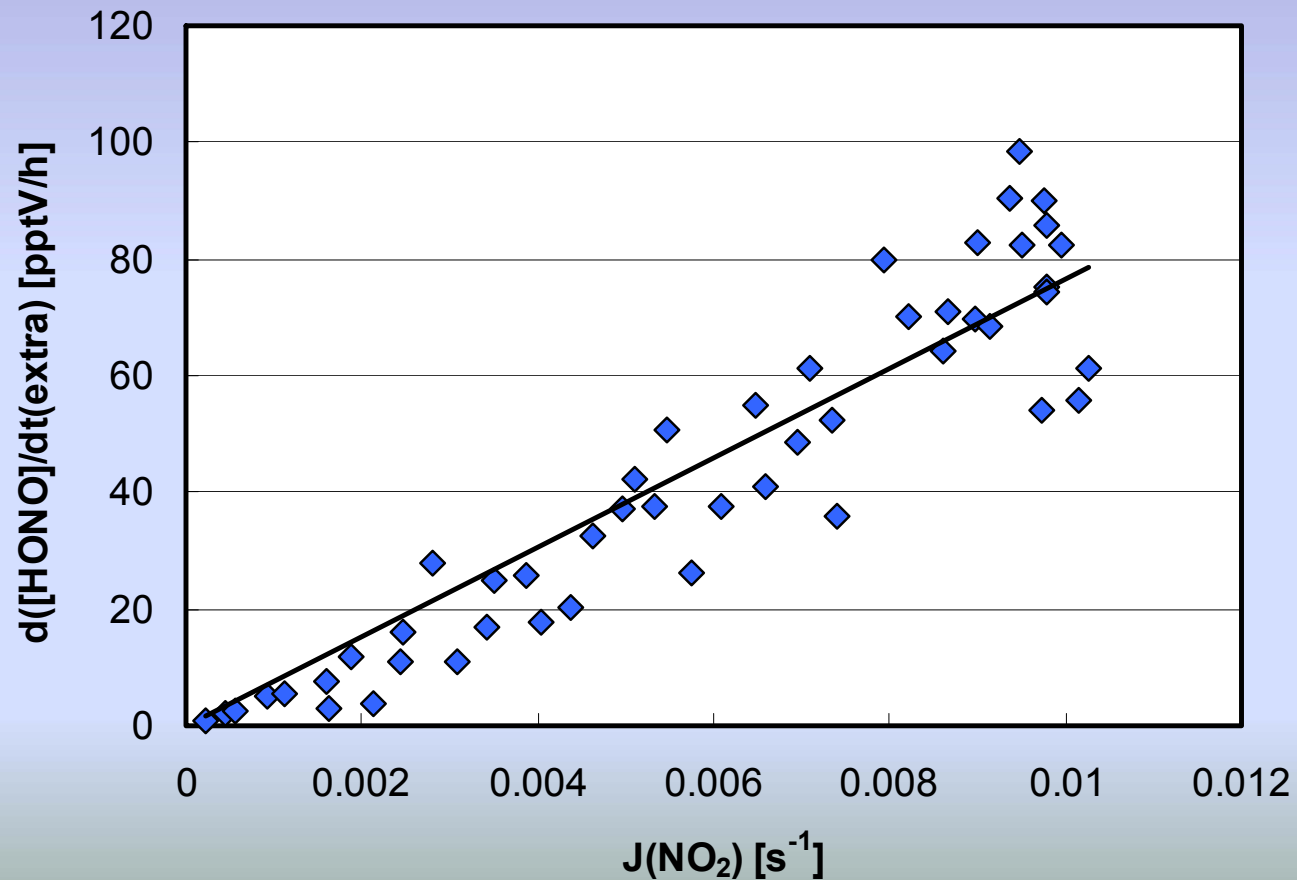
- Extra daytime HONO/OH source of up to 80 pptV/h
- Correlates with $J(\text{NO}_2)$



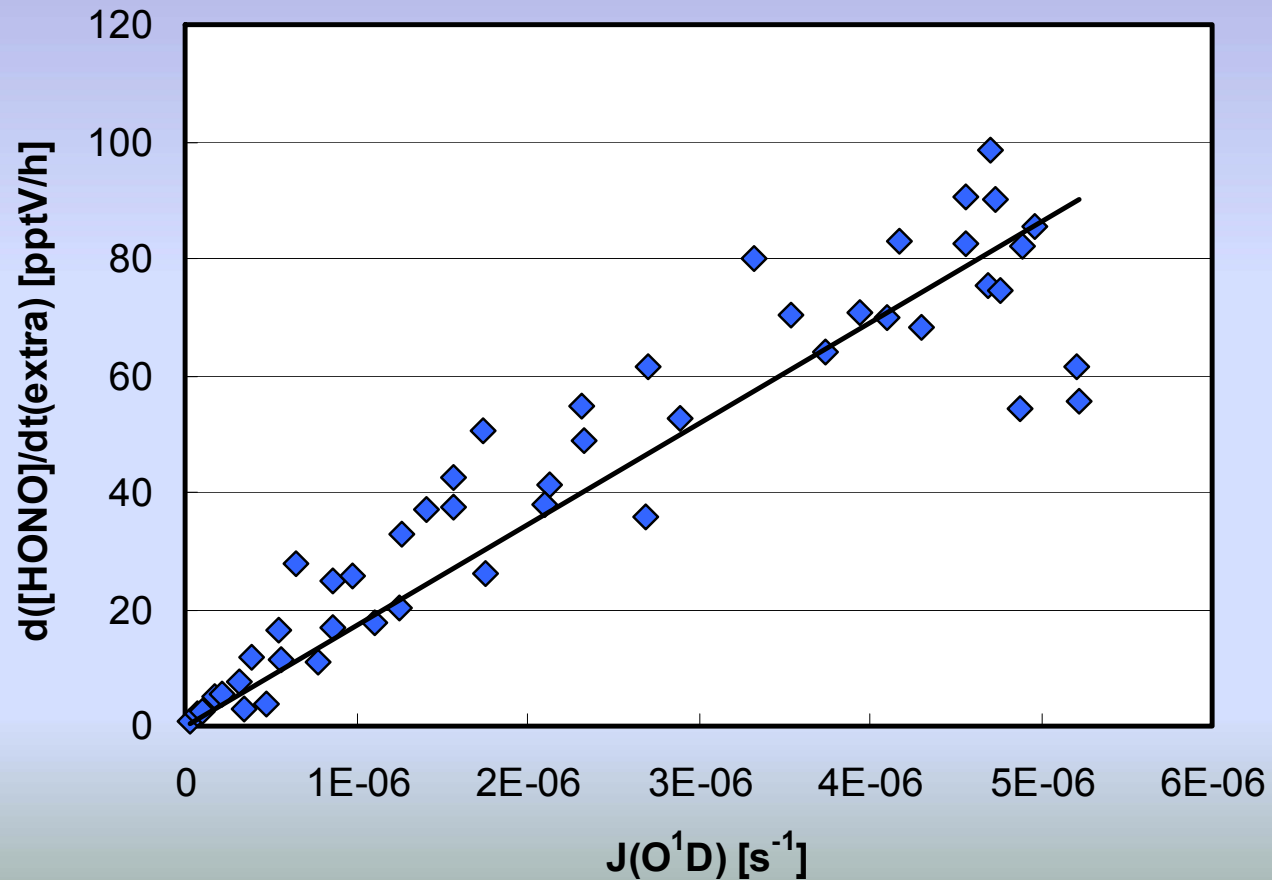
- Extra HONO/OH source >> OH source by O₃-photolysis



- Extra HONO/OH source correlates with $J(\text{NO}_2)$
 - $\text{NO}_2 + \text{HA} + h\nu$ correlates with $J(\text{NO}_2)$
 - nitrate-photolysis not...



- But correlates also with $J(\text{O}^1\text{D})$...
 - nitrate photolysis would correlate with $J(\text{O}_1\text{D})$



- Photochemical HONO formation observed
- But: Mechanism still not clear...
- Can be hopefully further clarified when still missing data ([HA], [nitrate], etc.) is available...

- HONO successfully measured under polar conditions for the first time by the LOPAP technique
- HONO/NO_x and HONO/NO_y in excellent agreement with other remote LOPAP data, but much lower compared to previous data from "wet chemical" instruments
- ➔ HONO] was overestimated in the past, in excellent agreement with recent LIF data from South Pole
- ➔ Interferences are a serious problem for "wet chemical" HONO instruments

- $[\text{HONO}]_{\text{exp.}} \gg [\text{HONO}]_{\text{theo.}}$
- Extra HONO source of up to 80 pptV/h quantified
- Much more important compared to the O_3 -photolysis
- Extra HONO source correlates with light intensity
- ➔ Photochemical source proposed in good agreement to other studies
- Formation mechanism still not clear...

Thank you for your attention

