HONO Measurements at Barrow, Alaska, using the LOPAP Technique

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Introduction

- ❑ Nitrous Acid is an important OH-source in polar regions:

  HONO + hν → OH + NO (1)

- ❑ Formation mechanism under discussion (*Zhou et al.*, 2001; *Stemmler et al.*, 2006):

  NO_3^- + hν → NO_2^- + O (+H^+ → HONO) (2)

  NO_2 + humic acids + hν → HONO + products (3)

- ❑ Doubts about reliability of polar "wet chemical" HONO measurements (*Kleffmann and Wiesen*, 2008)

Aim of the study

- ❑ Measurement of HONO by the LOPAP technique during OASIS/Barrow 2009 campaign

Experimental: The LOPAP®-instrument

- ❑ Wet chemical instrument (fast, selective reaction)
- ❑ No inlet lines used (external sampling unit, see Fig. 1)
- ❑ Two channel system to correct interferences (see Fig. 1)
- ❑ Excellent agreement with DOAS also during daytime (smog chamber/atmosphere, *Kleffmann et al.*, 2006).

⇔ In contrast to most other published intercomparison studies (typically much higher concentrations by the wet chemical instruments ➔ interferences!)

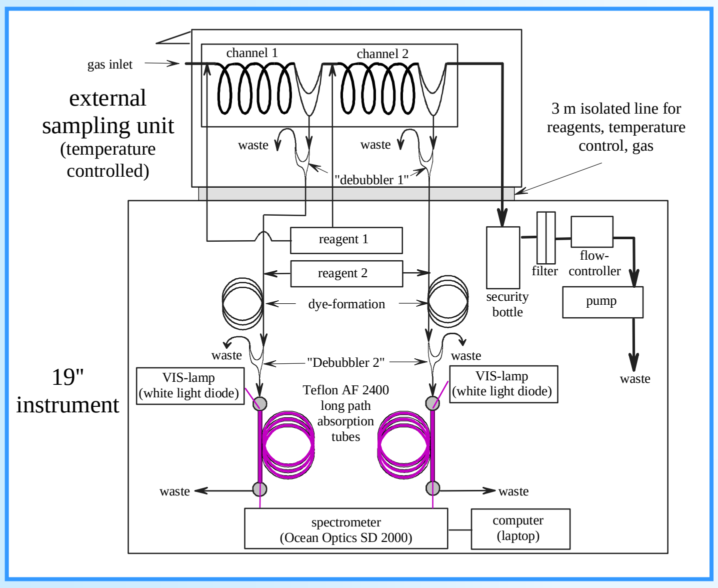
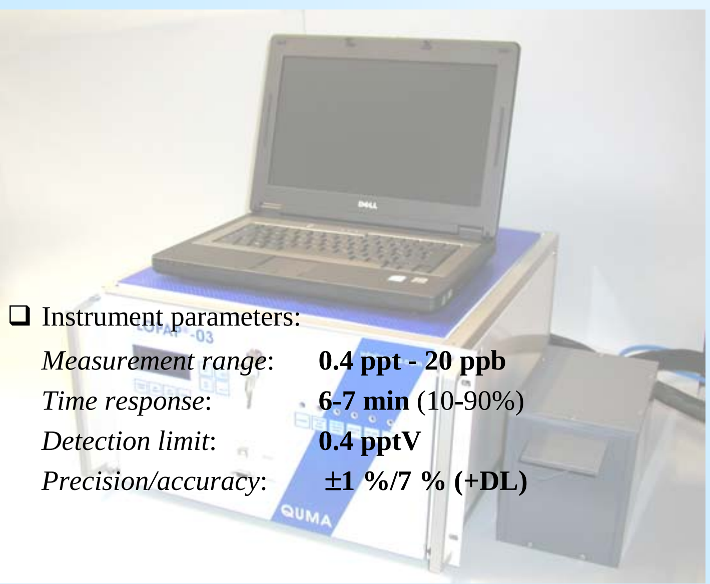


Fig. 1: *Scheme of the HONO-LOPAP instrument*



- ❑ Instrument parameters:

Measurement range:	**0.4 ppt - 20 ppb**
Time response:	**6-7 min** (10-90%)
Detection limit:	**0.4 pptV**
Precision/accuracy:	±1 %/7 % (+DL)

Measurement site

- ❑ OASIS Barrow, March 13th-April 14th, 2009

Fig. 2: *LOPAP measurement site with sampling unit*

Results

- ❑ **[HONO]: 1 - 600 pptV**
- ❑ **High HONO correlates with high NO_x/CO**

➔ **Emissions (combustion) on many days**

- ❑ **Average [HONO] for all (7) "clean" days 1-10 pptV**
- ❑ **HONO/NO_x = 5.3 %; HONO/NO_y = 1.0 % (clean)**

  Excellent agreement with other remote LOPAP measurements at mountains "Jungfraujoch" (4.6 %; 1.1 %) and "Zugspitze" (2.5 %; 1.0 %)

⇔ Much lower compared to other polar studies in which HONO/NO_x of 20-100 % was determined

➔ Significant interferences of wet chemical instruments are corrected for by the LOPAP instrument (*Kleffmann and Wiesen*, 2008)

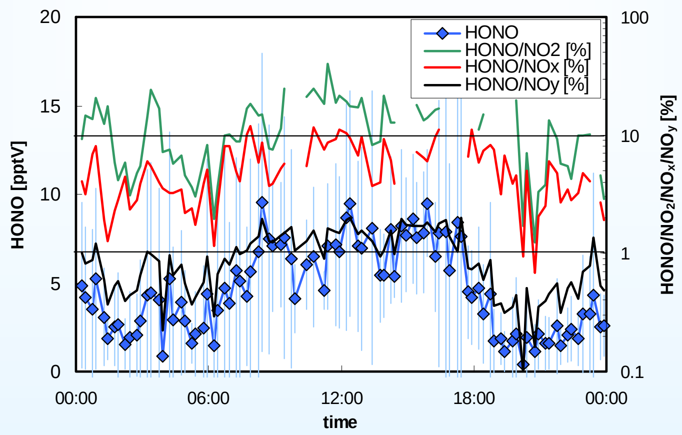


Fig. 3: *HONO, HONO/NO_2, HONO/NO_x, HONO/NO_y (average "clean" day)*

- ❑ **$[HONO]_{meas.}$>$[HONO]_{theo.}$** (*PSS/gas phase chemistry* and *PSS/gas phase chemistry + het. night-time source*)

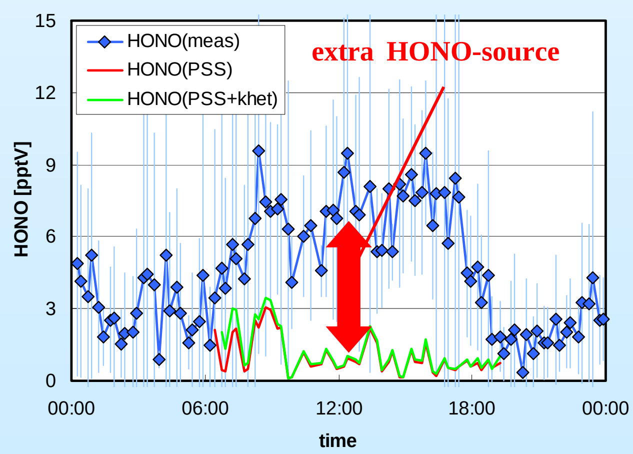


Fig. 4: *$[HONO]_{meas.}$ and $[HONO]_{PSS}$ (average "clean" day)*

Results (cont.)

- ❑ From the difference ($[HONO]_{meas.}$-$[HONO]_{PSS}$) ➔ net daytime production of HONO (= $d[HONO]/dt_{(extra)}$ = net production of OH by HONO photolysis).

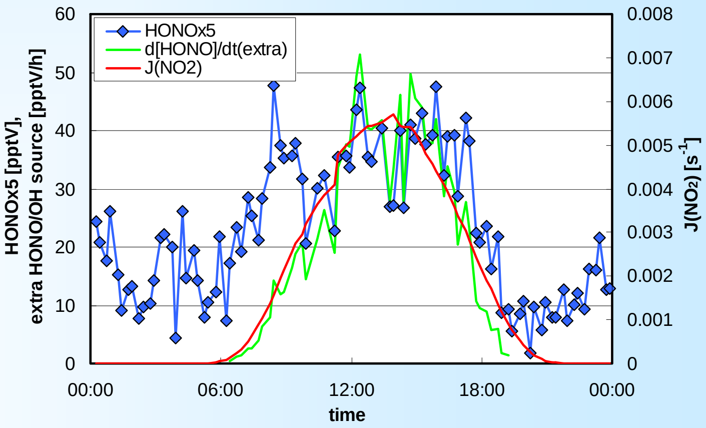


Fig. 5: *HONO, J(NO_2), $d[HONO]/dt_{(extra)}$ during daytime*

- ❑ **Daytime HONO source ~ J(NO_2)**

➔ **Photochemical sources proposed (0-50 pptV/h)**

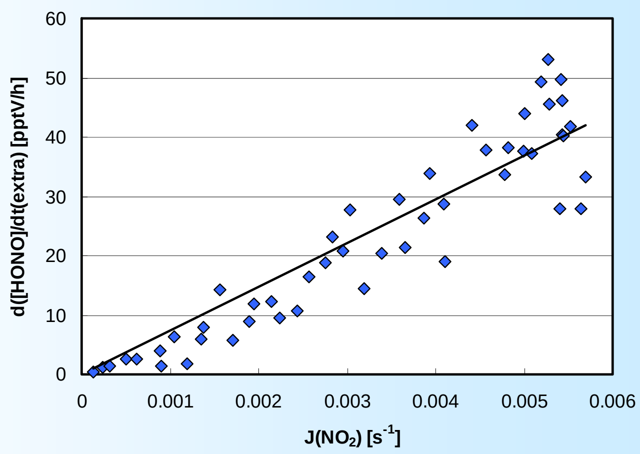


Fig. 6: *Correlation of daytime HONO source with J(NO_2)*

Conclusions

- ❑ Low HONO concentrations on clean days
- ❑ HONO maximum during daytime
- ❑ Low HONO/NO_x, HONO/NO_y in contrast to other polar "wet chemical" HONO measurements

➔ Interferences are corrected for by the LOPAP

- ❑ Net daytime HONO-/OH-source correlates with J(NO_2)

➔ Photochemical sources proposed

- ❑ Correlation with other parameters ([HA], nitrate, etc.) may help to identify potential sources (ongoing...)

References:

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