

**The LOPAP technique**  
*(Long Path Absorption Photometer)*

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- HONO was demonstrated to be a major source of OH radicals in the lower atmosphere → “new daytime sources” postulated
  - **New daytime source**  $\propto \Delta(\text{HONO}_{\text{measured}} - \text{PSS})$ ; both are low, difference can be small
- Introduction**
- Sensitive, precise and accurate measurements of nitrous acid are of high importance
  - BUW developed a new instrument (started in 1999...)

## **LOPAP-Technique (long path absorption photometer)**



## **LOPAP-Technique** (*long path absorption photometer*)

### ○ Chemical instrument:

HONO sampled by a fast, selective chemical reaction in a stripping coil, converted into an azo dye, which is photometrically detected in long path absorption

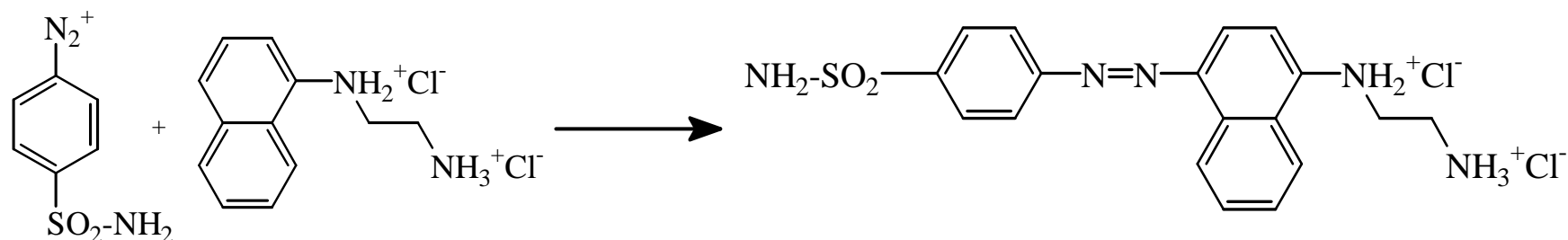
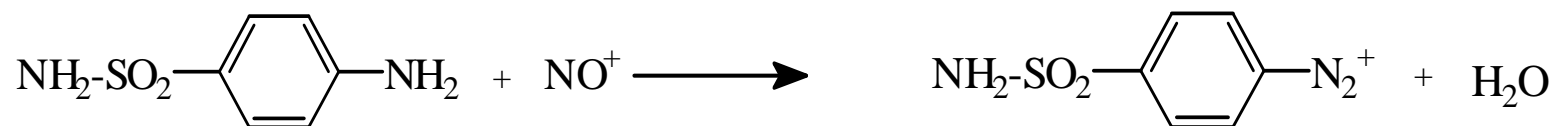
*published in:*

Heland, et al., *Environ. Sci. Technol.*, 2001, **35**, 3207-3212;

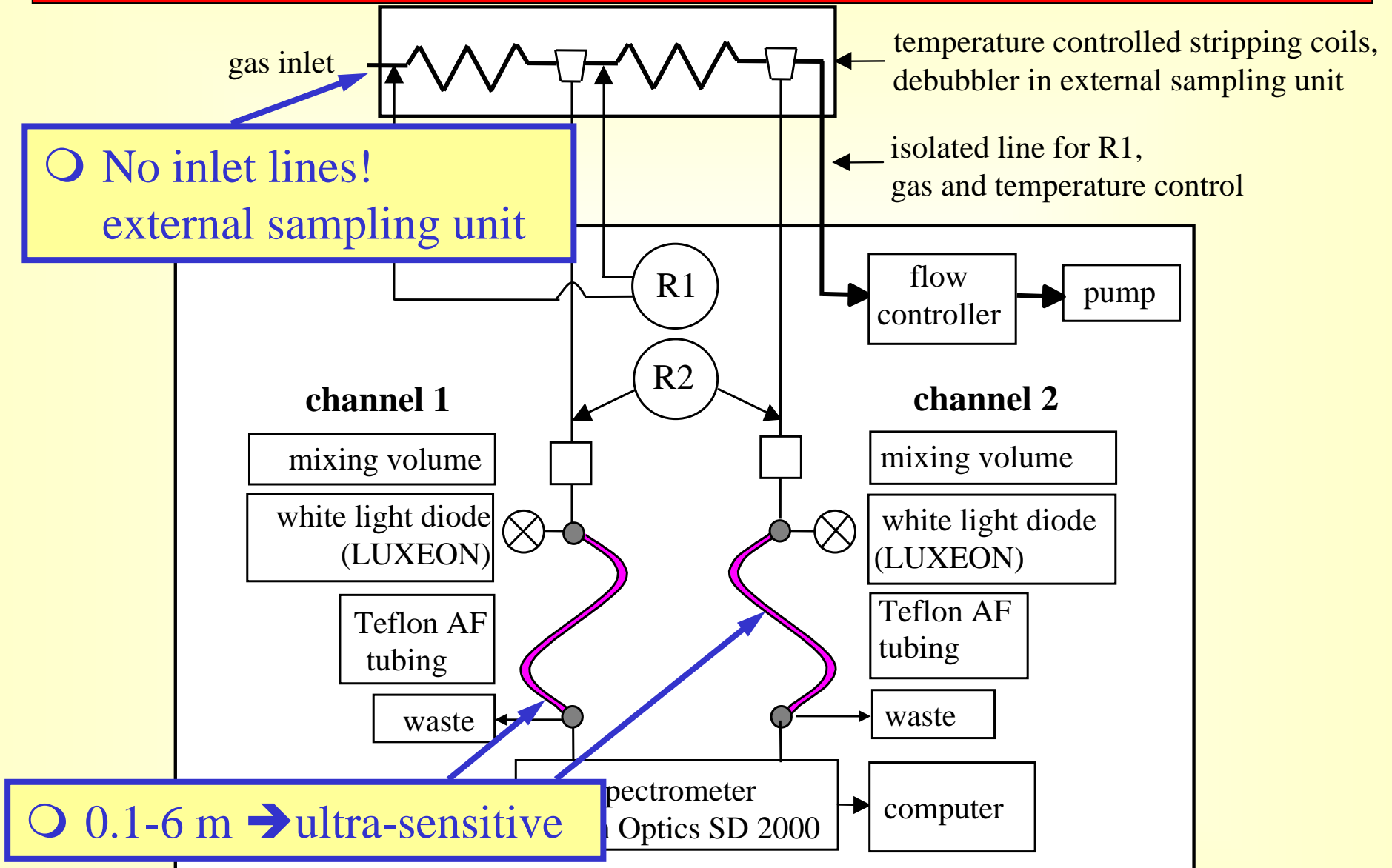
Kleffmann et al., *Environ. Sci. Pollut. Res.*, 2002, **9**, 48-54;

Kleffmann et al., *Atmos. Environ.*, 2006, **40**, 3640-3652

○ Reactions:

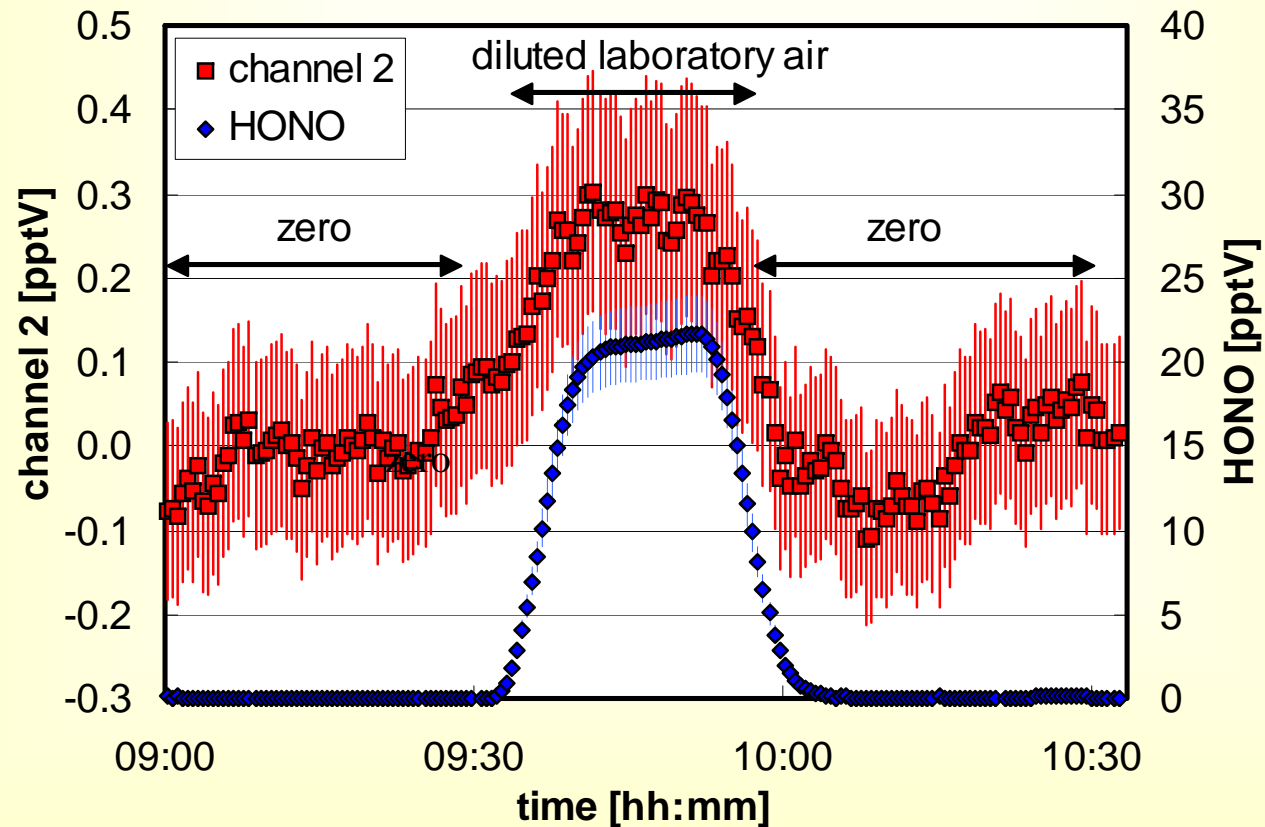


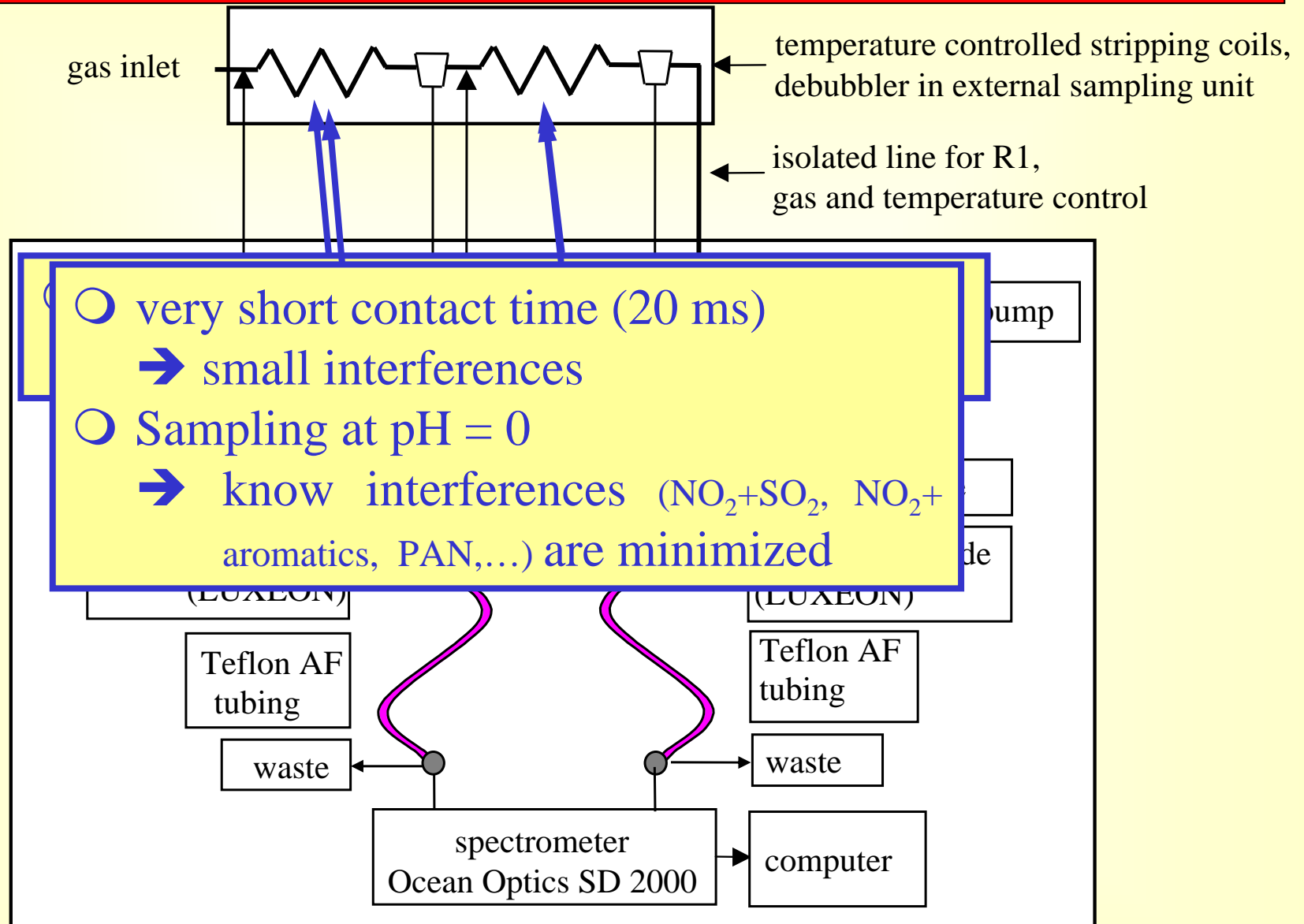
Formed azo-dye strong absorber:  $\epsilon=50.000 \text{ M}^{-1} \text{ cm}^{-1}$ , 540 nm)



## LOPAP-Technique (*long path absorption photometer*)

- DL: 0.2-2 pptV
- Time resolution: 7-2 min (10-90 % signal)





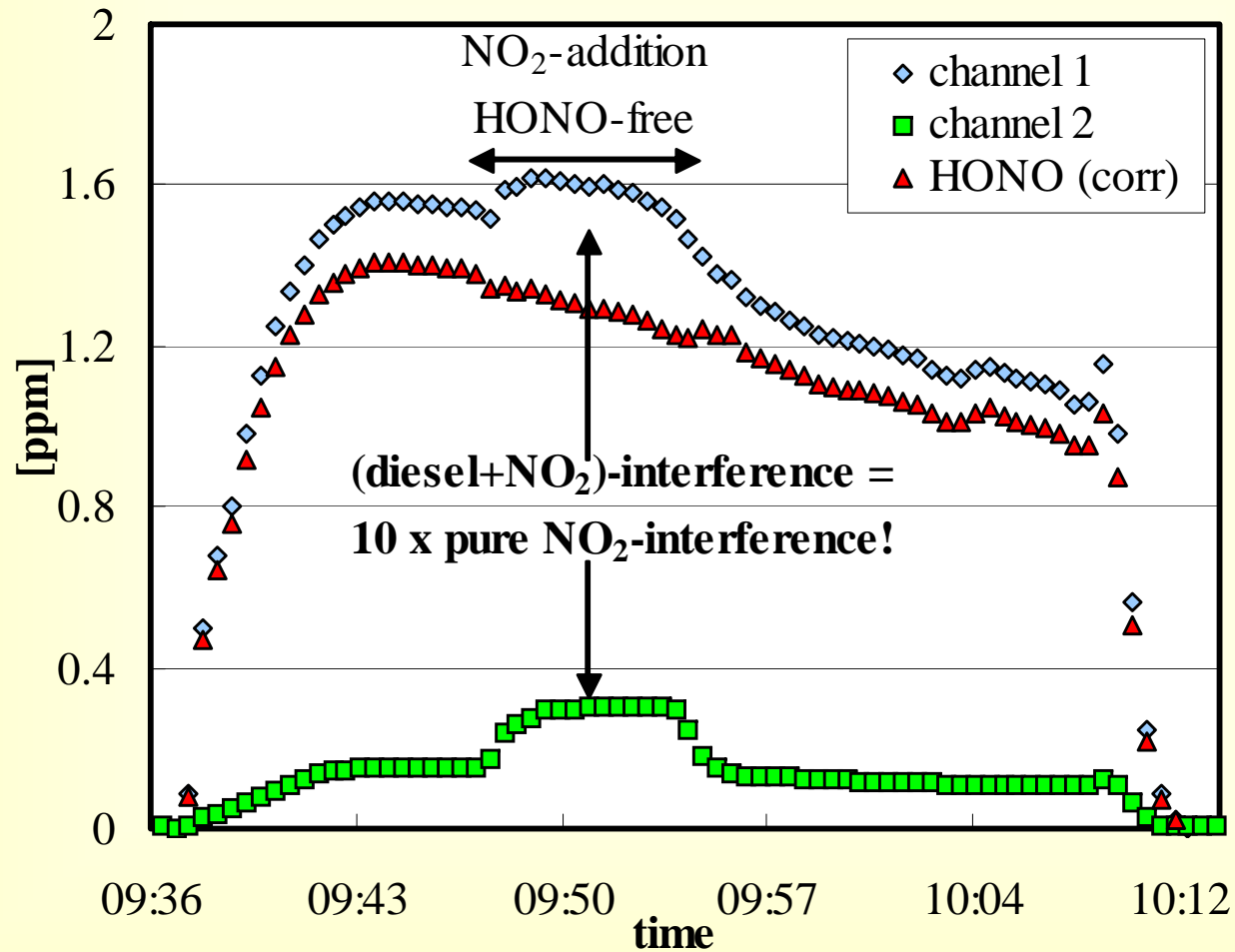
- Several interferences were quantified in the laboratory:

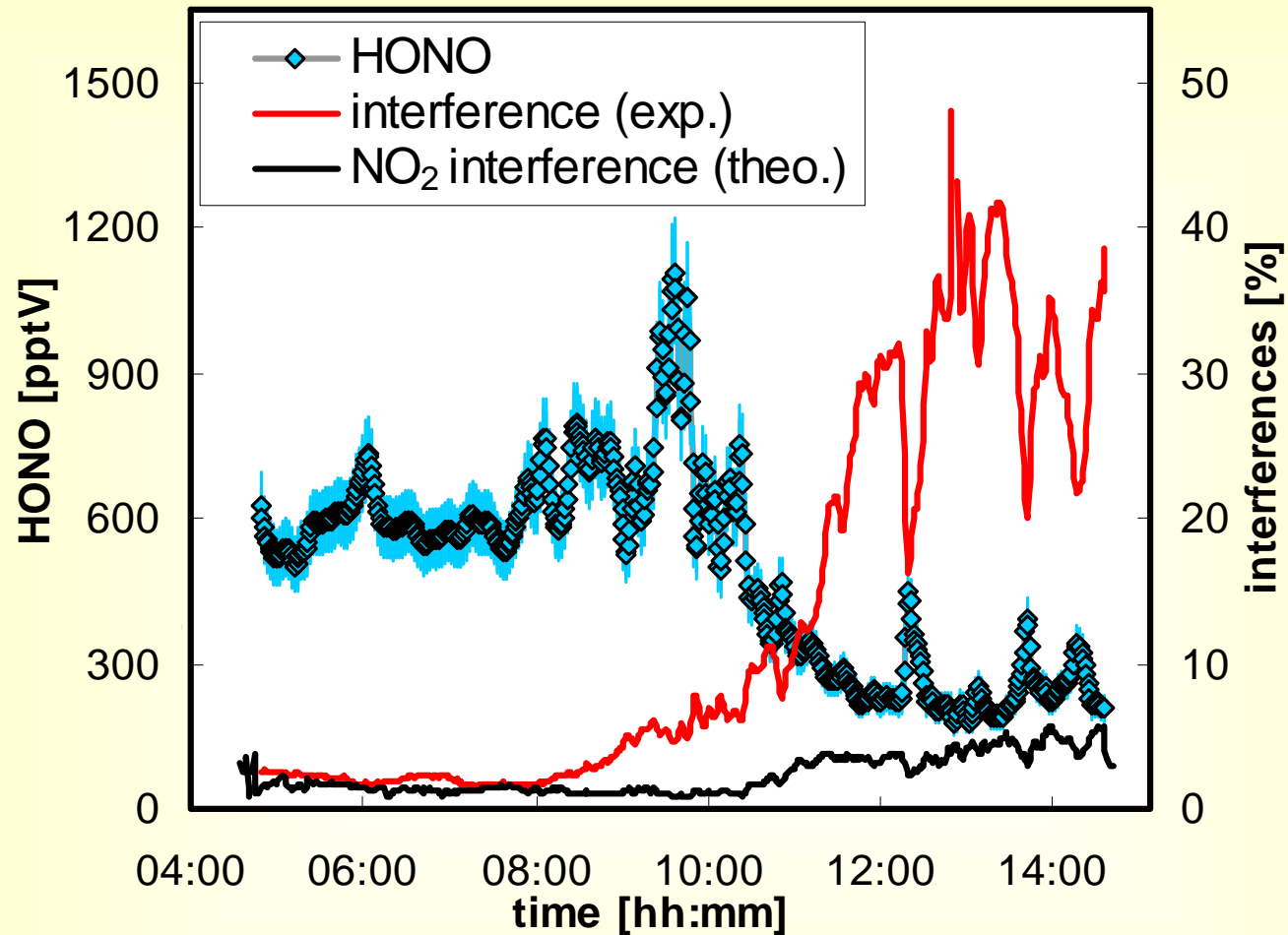
*NO, NO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>, O<sub>3</sub>, O<sub>3</sub>+HONO, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>+HONO,  
NO<sub>2</sub>+SO<sub>2</sub>, HNO<sub>3</sub>, HNO<sub>3</sub>+HCHO, PAN, organic nitrates,  
NO<sub>x</sub>+ethene, NO<sub>x</sub>+toluene, NO<sub>x</sub>+n-butane, NO<sub>2</sub>+o-cresol,  
NO<sub>2</sub>+diesel exhaust, particle nitrite...*

**Interferences**

- ➔ *Not measurable* or can be *corrected* for by the two-channel design of the instrument

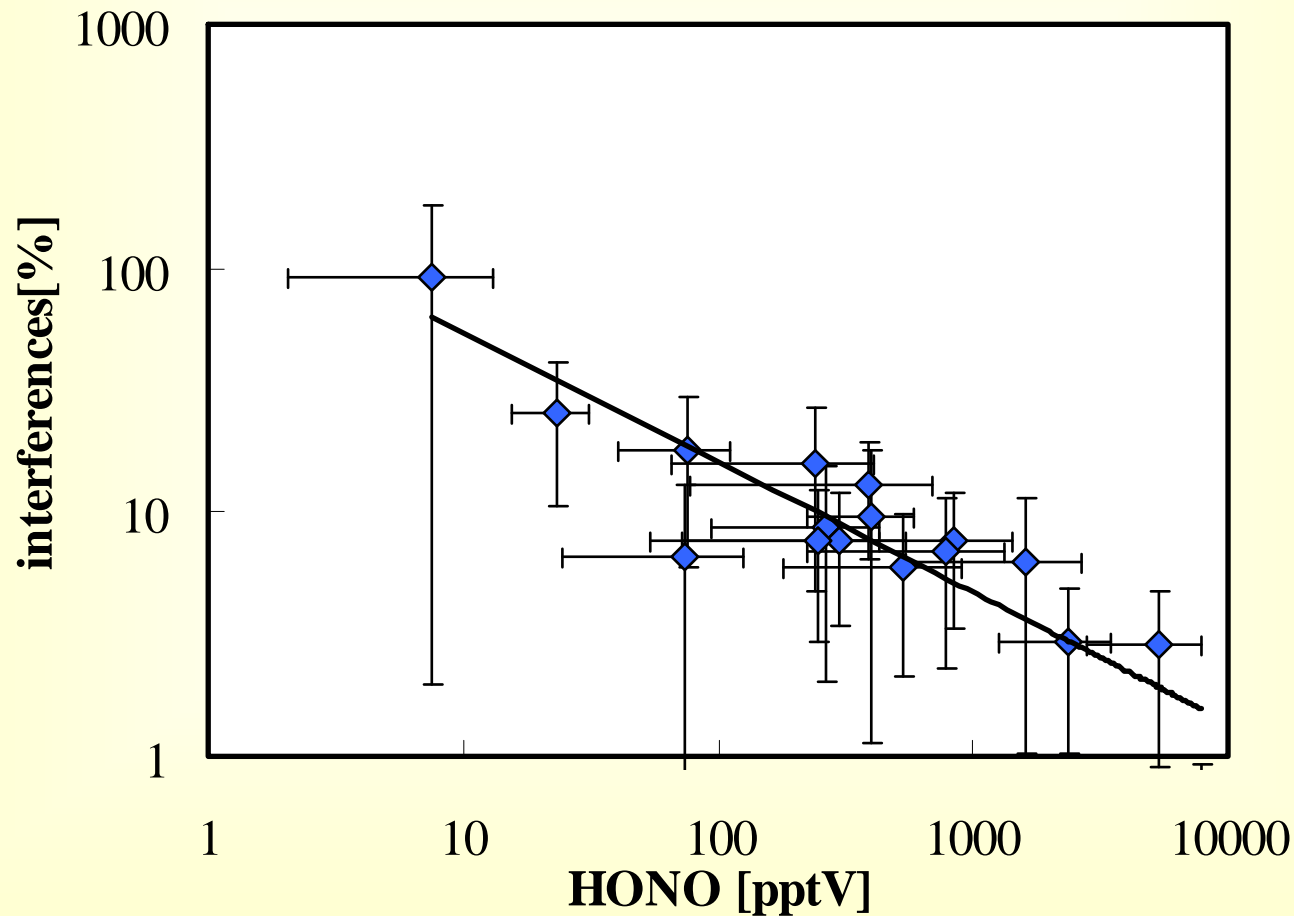
- 💣 NO<sub>2</sub>+diesel exhaust interference significant! 😊 Is well corrected!  
In contrast to a WEDD (see *Gutzwiller et al., 2002*)



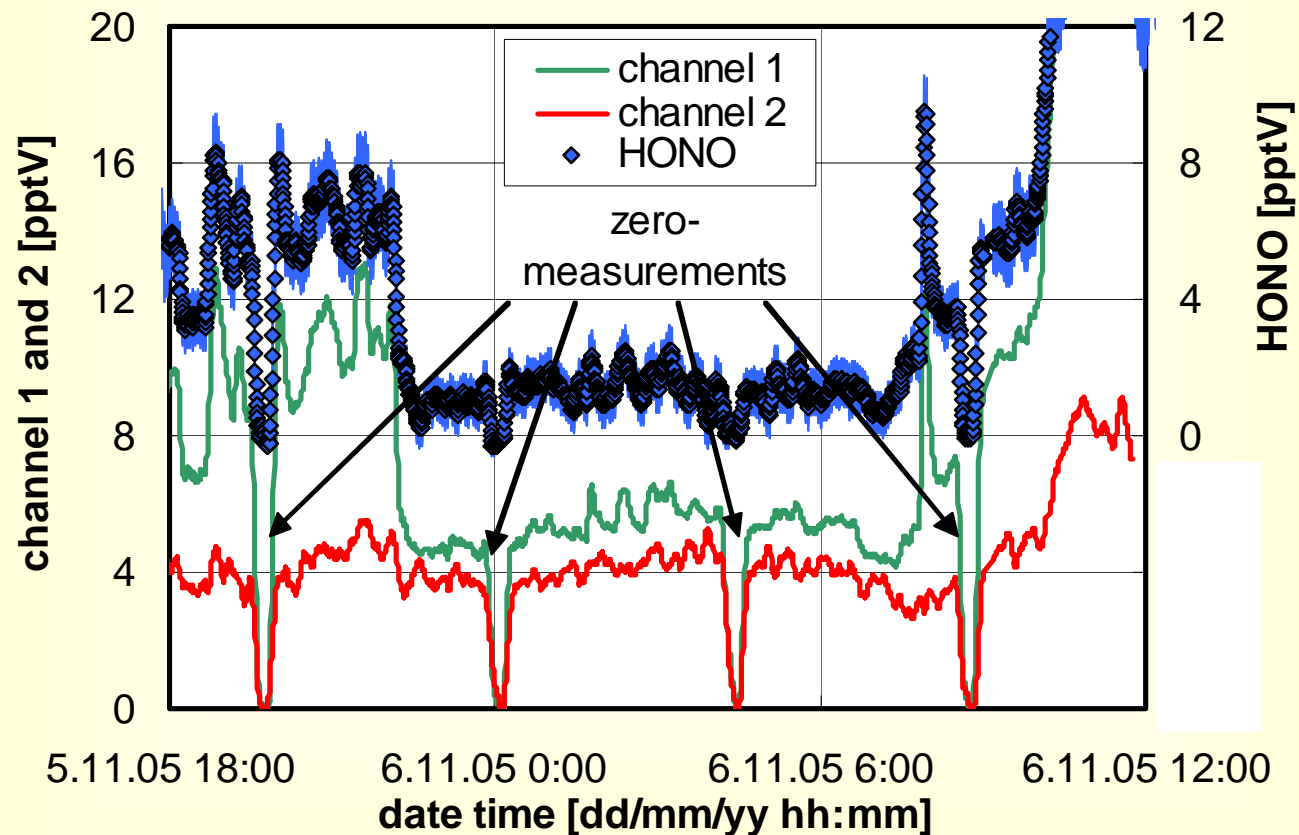


○ Measured interferences cannot be explained by known (pure) interferences

- Measured interferences increase with decreasing HONO-concentration, can explain deviations from intercomparison studies...



- Interferences are of special importance for remote conditions (here up to a factor of 4 correction...)

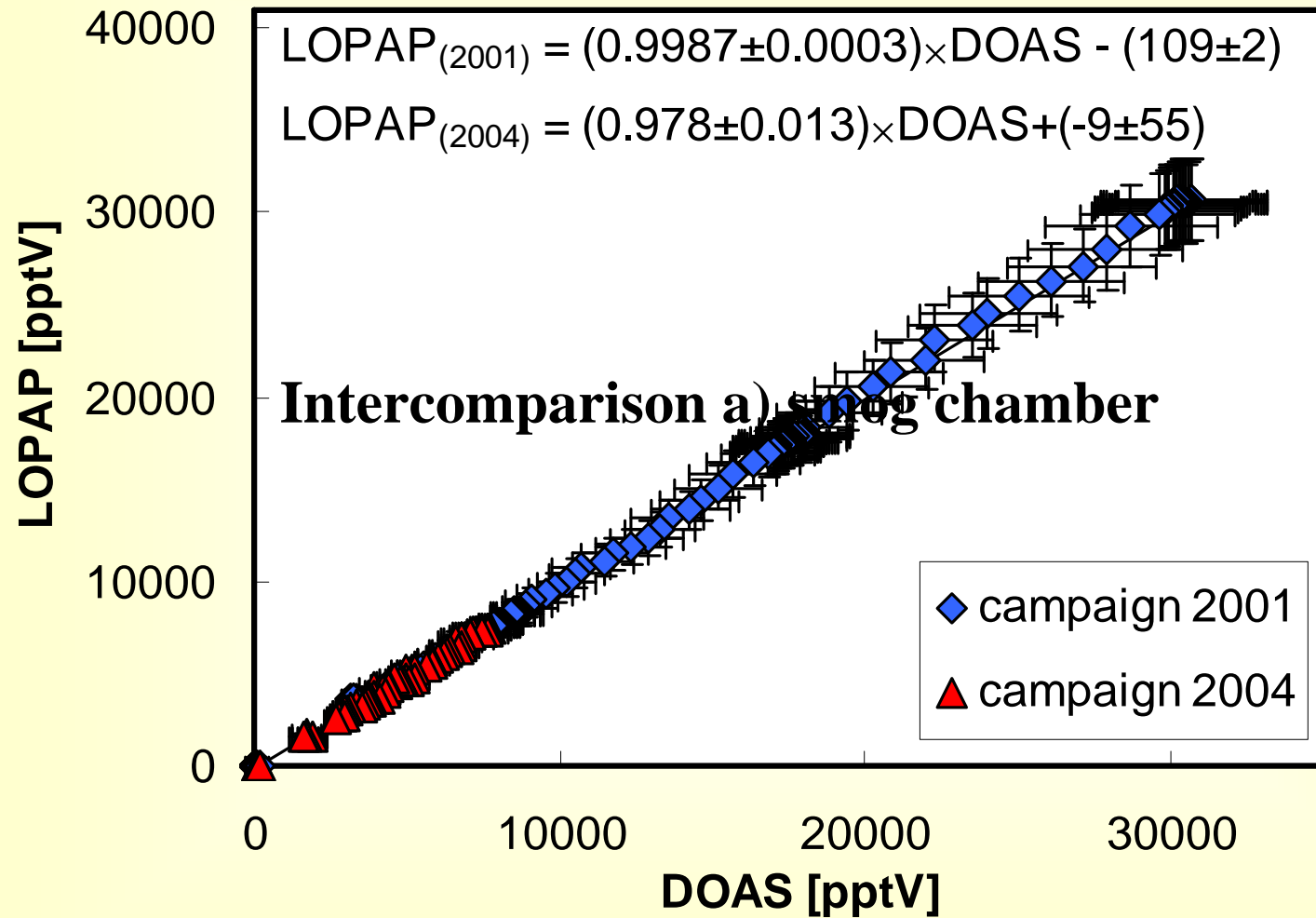


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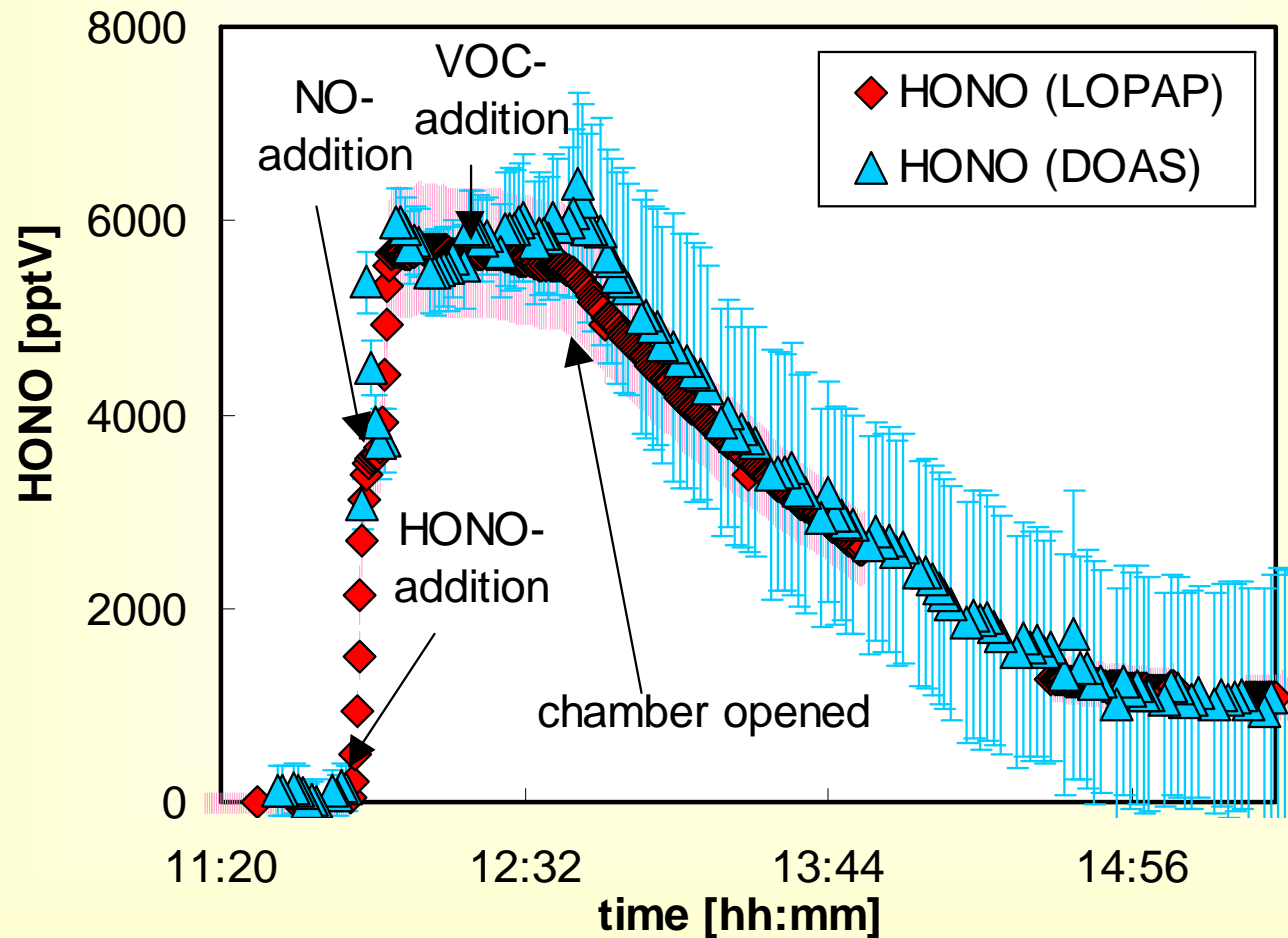
*NO, NO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>, O<sub>3</sub>, O<sub>3</sub>+HONO, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>+HONO,  
NO<sub>2</sub>+SO<sub>2</sub>, HNO<sub>3</sub>, HNO<sub>3</sub>+HCHO, PAN, organic nitrates,  
NO<sub>x</sub>+ethene, NO<sub>x</sub>+toluene, NO<sub>x</sub>+n-butane, NO<sub>2</sub>+o-cresol,  
NO<sub>2</sub>+diesel exhaust,...*

- ➔ *Not measurable or can be corrected for by the two-channel design of the instrument*
- 💣 unknown interferences might be still significant...
- ➔ Intercomparison with an optical instrument under “real world” conditions

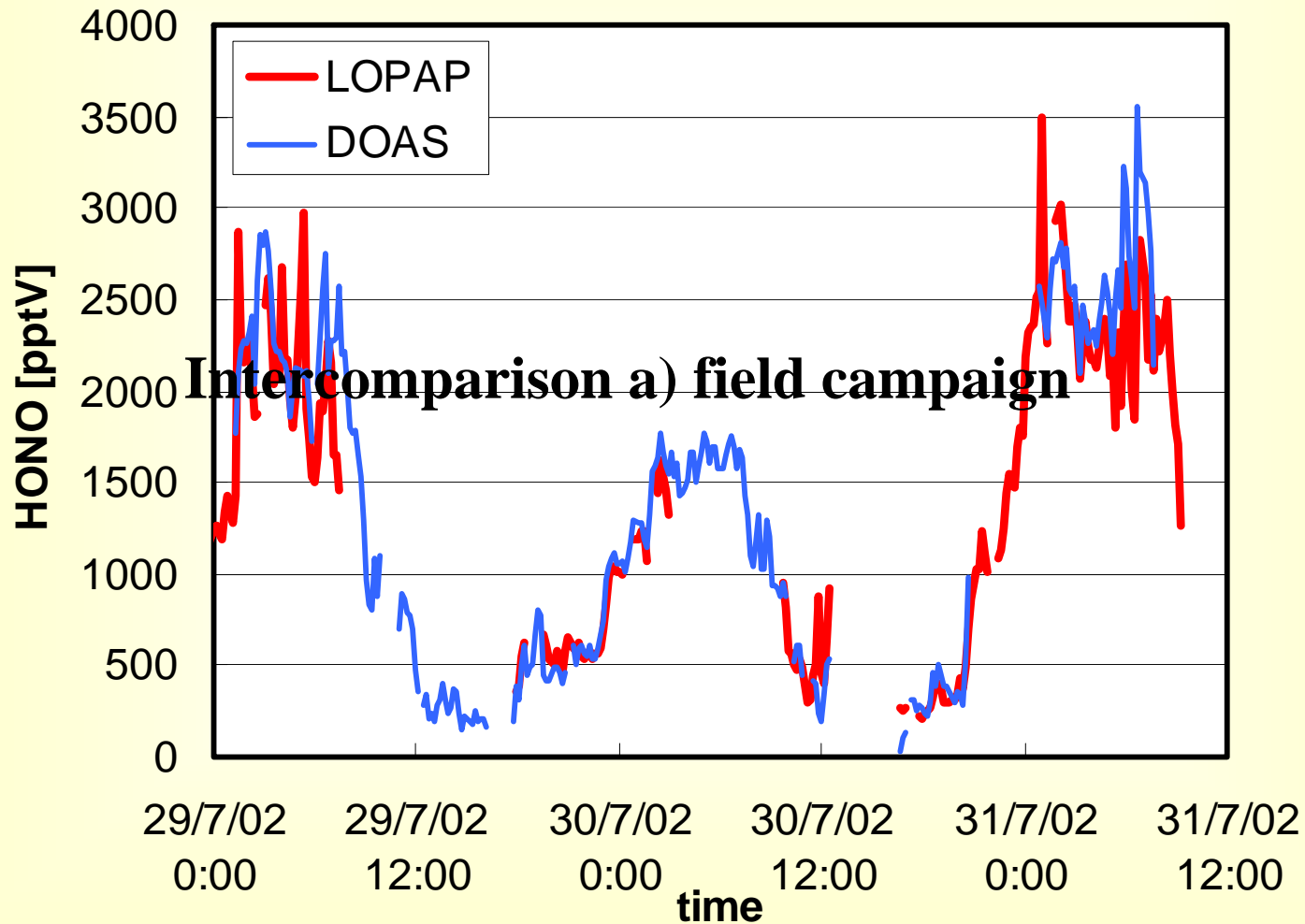
☺ Pure HONO/NO<sub>x</sub> mixtures in the dark (EUPHORE)



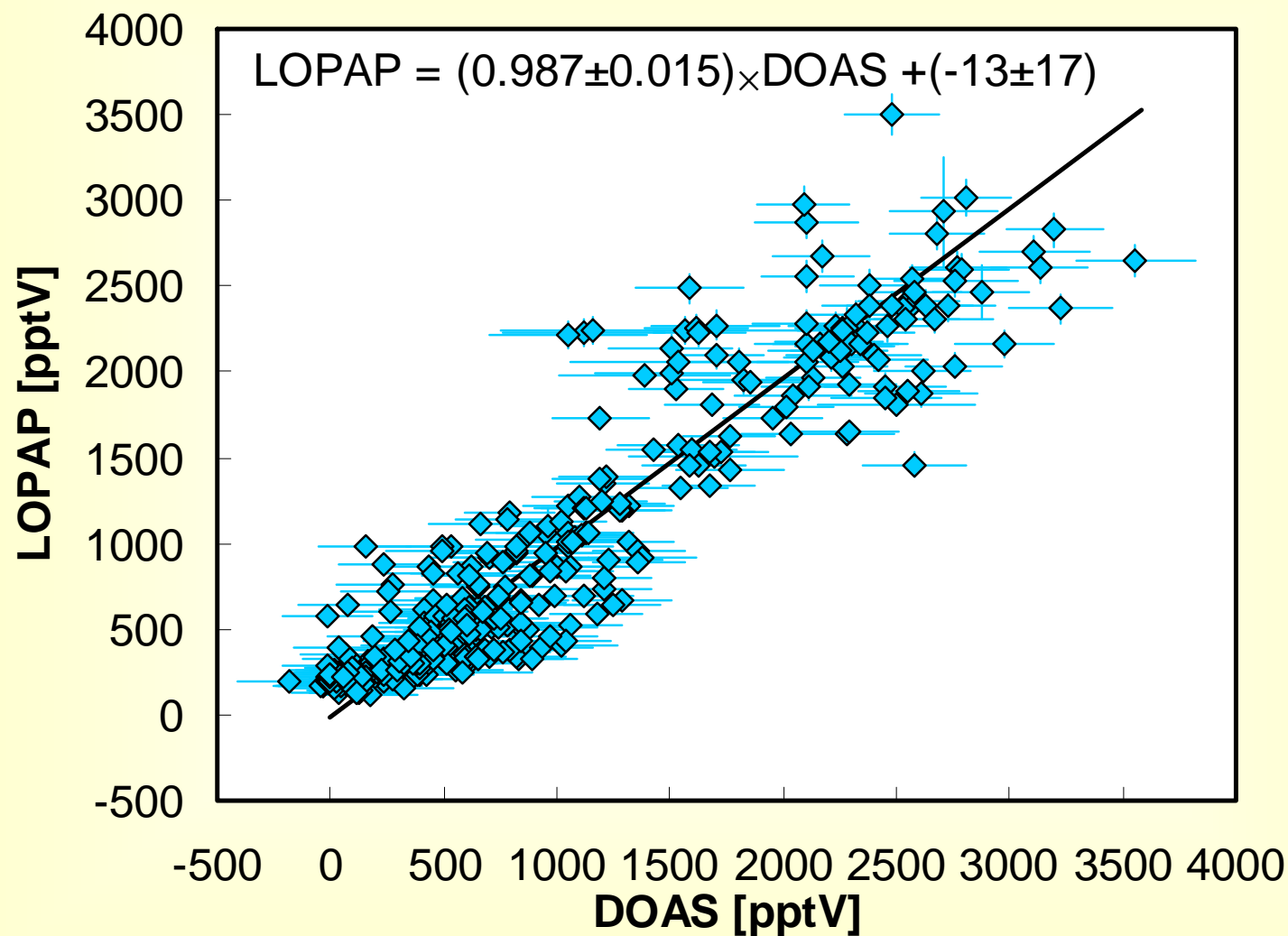
☺ Photosmog experiment in a smog chamber (200 ppbv NO<sub>x</sub>, 150 ppbv toluene, 450 ppbv ethene, 450 ppb n-butane + hv)



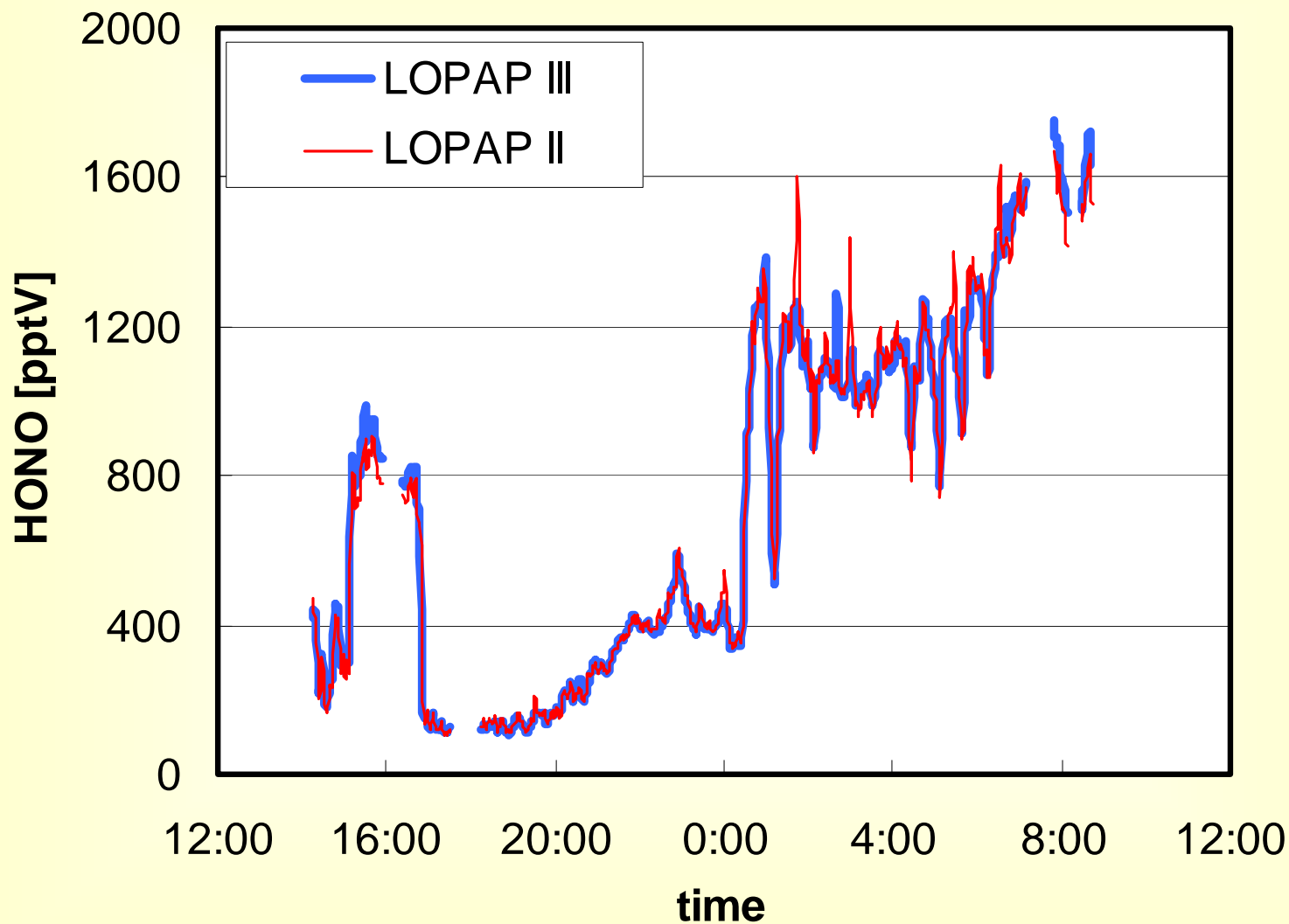
- ☺ Field measurement in Milan (FORMAT) using an open White mirror system for the DOAS (→ same air mass)



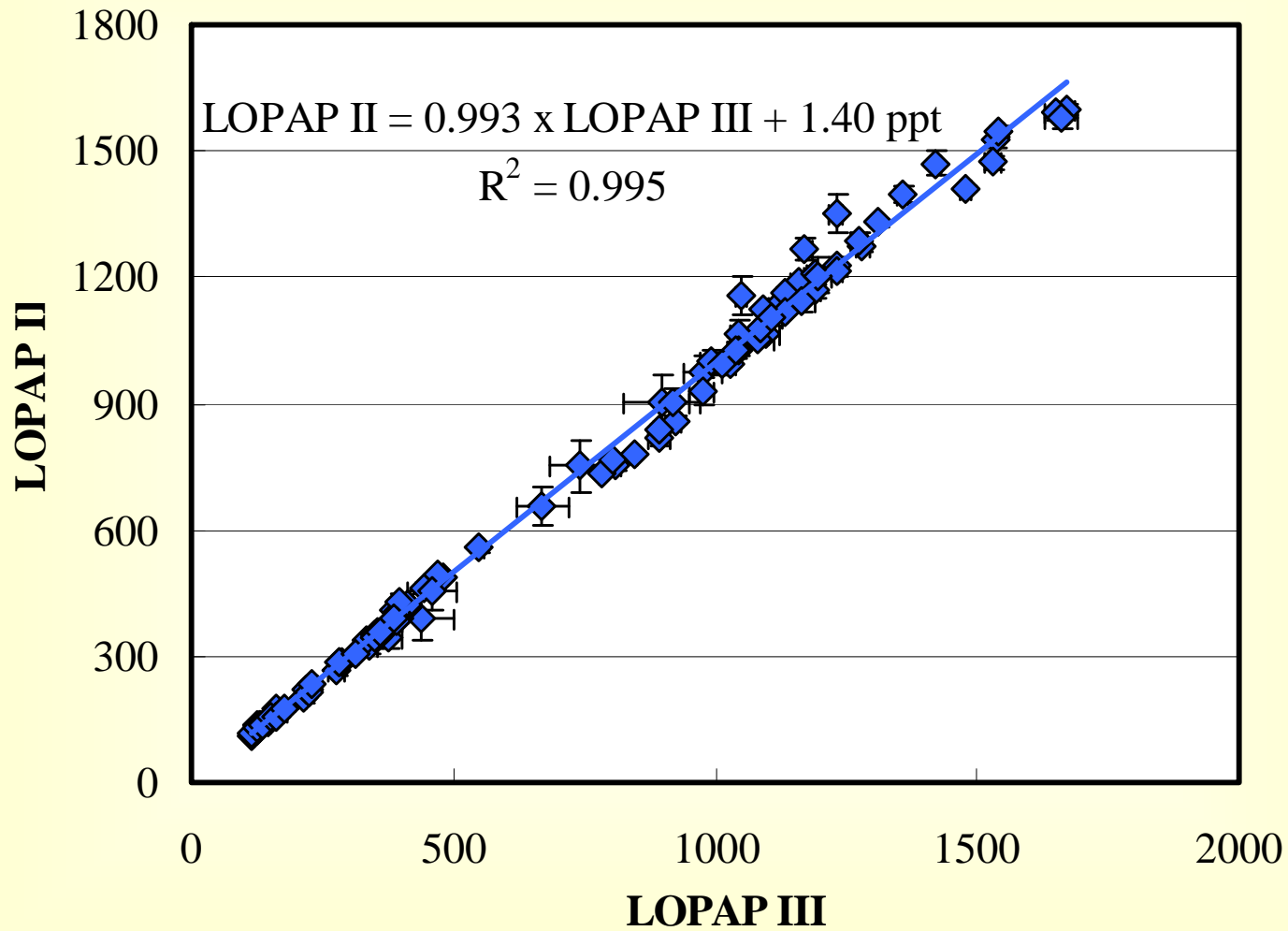
☺ All simultaneous 10 min data:



☺ Intercomparison between two LOPAP instruments: high precision



☺ Intercomparison between two LOPAP instruments: high precision



- ☺ Excellent agreement between the LOPAP and the DOAS instrument for all conditions including daytime measurements
- 💣 Interferences of LOPAP instrument are significant during the day

### **Summary LOPAP**

- ☺ Are corrected for by the two-channel design of the instrument
- ➔ Validation of chemical instruments against an optical instrument free of sampling artefacts is of paramount importance

- European Commission within the NITROCAT project (Contract no. EVK2-1999-00025),
  - European Commission within the FORMAT project (EVK2-CT-2001-00120)
- Acknowledgements LOPAP**
- Deutsche Bundesstiftung Umwelt (DBU) under contract No. 12634. R.
  - QUMA Elektronik & Analytik GmbH, Wuppertal

- Lower sensitivity set-up proposed (1 m optical path-length, 2 min time resolution), depends on the concentration range...
- Measurement range: 5 ppt (DL) - 200 ppb
- Accuracy:  $\pm 7\%$  (+DL)
- Precision:  $\pm 1\%$  (+DL)
- **Set-up LOPAP in EUPHORE**  
19'' instrument  $< 1.5$  m below the chamber floor, external sampling unit in the chamber, one connection line (3 cm OD) to the chamber (similar to the EUPHORE-LOPAP)
- One day needed for set-up
- Ca. 3x during the campaign access to the chamber necessary (check gas flow, liquid flow at the external sampling unit...)

**Thank you for your  
attention!**