European NOx-intercomparison at the observatory Hohenpeißenberg 10.-21. October 2016

Holla, R.; Kubistin, D.; Plass-Dülmer, C.; Englert, J.; Weyrauch, D. (1); Vokoun, M.; Silhavy, J. (2); Cristofanelli, P.; Calzolari F. (3); Walden, J.; Monto, M. (4); Berkes, F.; Houben, N. (5); Pöhler, D.; Lutz, E. (6); Putaud, J.; Lagler, F. (7);Tison, E.; Salameh, T., Sauvage, S. (8); Gros, V.; Bonnaire, N. (9); Spindler, G.; Rabe, R. (10), MOHp side-by-side-intercomparison NO_x-ACTRIS Team (1) and Rohrer, Franz (11)

A total number of 11 European laboratories (6 countries, 17 instruments) participated in the ACTRIS NO_x side-by-side (s-b-s) intercomparison activity organised and hosted by DWD Hohenpeissenberg in October 2016. All instruments were connected to one common ring manifold supplied either with synthetic mixtures or ambient air. FZ-Juelich (WCC-NO_x) acted as reference laboratory at the end of the manifold. Various synthetic mixtures with mixing ratios between zero and 40 ppb for NO and NO_2, as well as ambient air, encountered a wide range from clean (<0.5 ppb NO_x) to polluted (several 10 ppb NO_x) conditions. Interferences due to NO_y species, alkenes and glyoxal were tested. Most of the participating instruments used chemiluminescence detection (CLD) for NO coupled with blue-light converter (BLC) for NO_2, or molybdenum converter for NO_2+. Additionally, instruments took part using optical techniques with NO_2 & NO iterative cavity enhanced DOAS (ICAD) and NO_2 cavity attenuated phase shift (CAPS).

Institute		Port	CLD-BLC	CLD-Mo	CLD-Au	CAPS	ICAD
HPB	DE	1a	2		1	1	
IAGOS	DE	2a	1				
CHMI	CZ	2a		2			
MD	FR	2b		1		1	
SIRTA	FR	4b	1				
IPR	EU	5b		1		1	
FMI	FI	6b	1				
TROPOS	DE	7b	1				
IUP-HD	DE	8b					1
ISAC	IT	10b	1				
FZJ	DE	11b	1				
total: 11	6		8	4	1	3	1 / 17

CLD: ChemiLuminescence Detector
BLC: Blue Light Converter
Mo: Molybdenum converter
Au: Gold converter
CAPS: Cavity Attenuated Phase Shift
ICAD: Iterative Cavity Enhanced DOAS

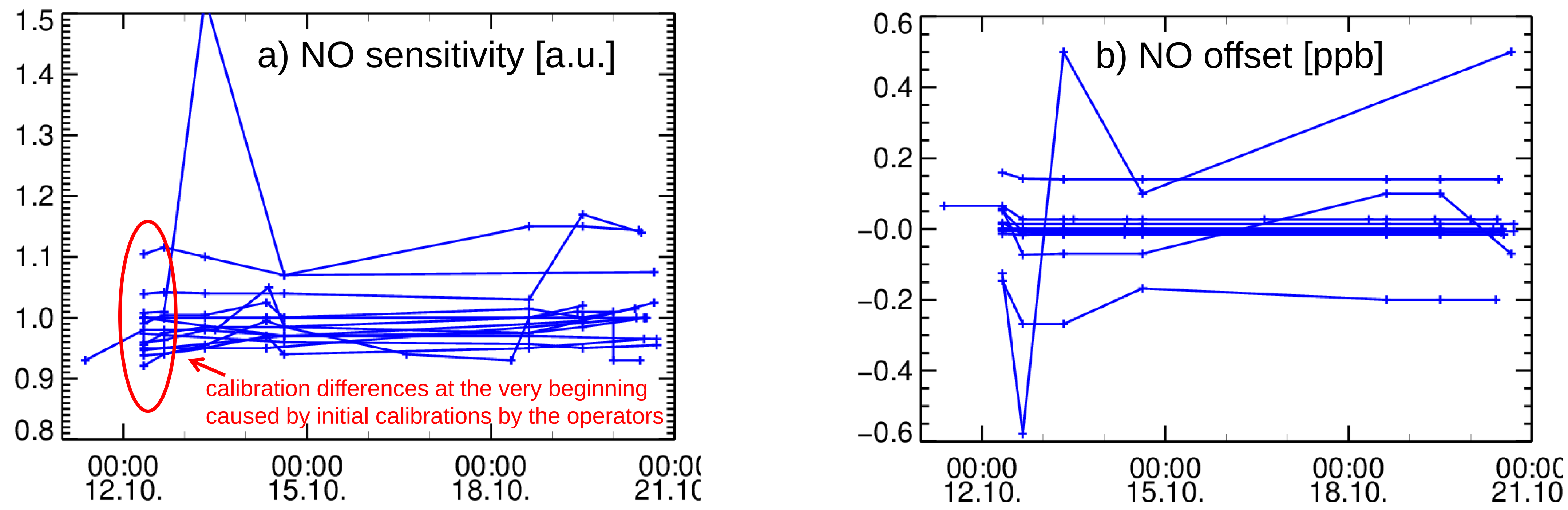

Figure 1: Stability of the instruments sensitivities and offsets over the whole campaign. Each instrument was calibrated with its own station calibration device using a common NO standard and the same zero air supply. After these individual calibrations the sensitivity change was tracked frequently by using a constant concentration of NO (30 ppb) and dry air over the common ring manifold. a) The ratios of individual sensitivities and the sensitivity of WCC/FZJ reference instrument over 10 days deviated about ±10 % under **dry zero air** conditions. b) The absolute offsets deviated about several hundred ppt under **dry zero air** conditions.

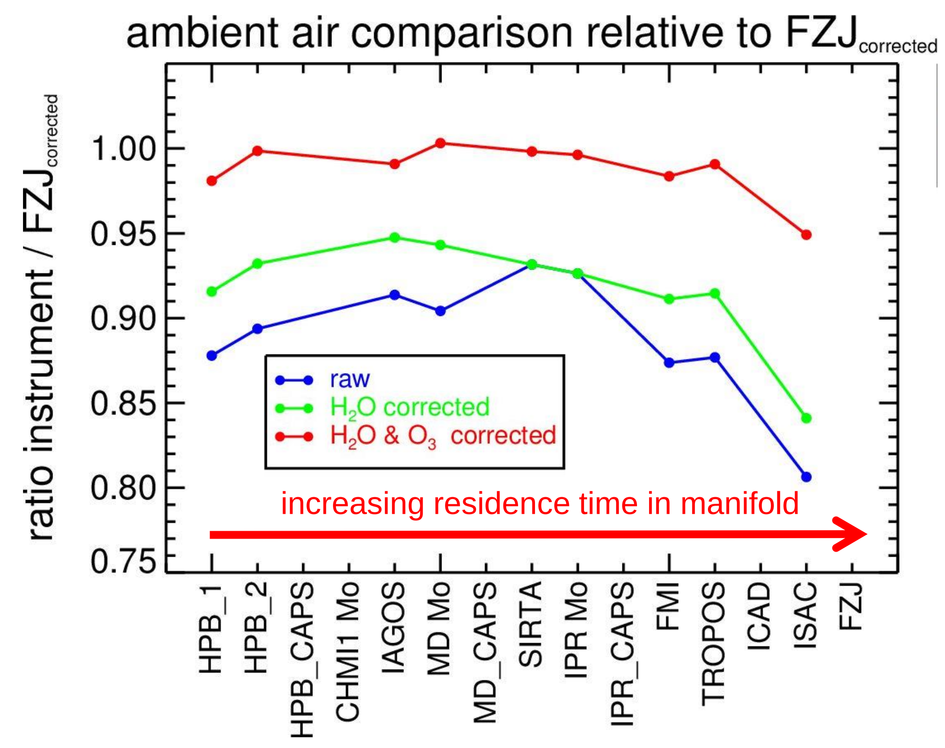

Figure 2: Comparison of the instruments during two days of **ambient air** measurements. The plots show the slopes of the correlations between individual instruments and WCC/FZJ reference instrument. Blue: without corrections applied, green: with water vapour corrections applied, red: both water and O_3 correction applied. Applying the corrections reduces the standard deviation between all instruments by a factor of three.

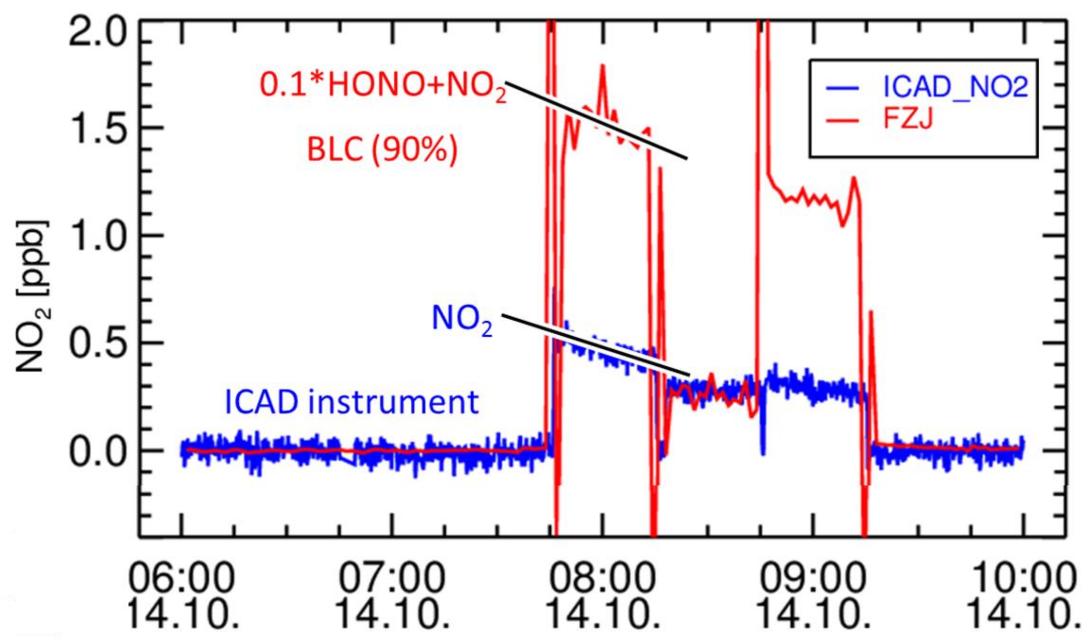

Figure 3: Example of NO_2 signals detected by ICAD and FZJ CLD during a HONO interference experiment. ~11 ppb HONO, NO and a small portion of NO_2 were injected into the manifold. Between 8:15 and 8:45 HONO was removed by an aqueous solution of NaOH. ICAD is not sensitive to HONO and can be regarded as a reference for NO_2. FZJ CLD shows significant interferences of 10% of HONO. The time decay is due to the depletion of the HONO source.

Data Quality Objectives (DQO) as defined in the GAW Measurement Guidelines

uncertainty (1 hour, 2σ)[2]	NO: 8 pmol/mol or 3% NO_2:15 pmol/mol or 5%

[2] which ever is the larger

Instrument	HONO interference [%]	PLC/BLC efficiency	NAFION/CAPS/Molybdenum (Mo)/Au-Converter
CHMI1	98.8	-	Mo
CHMI2	0*	-	Nafion, Mo
FMI	0.4	41%	
FZJ	9.3	92%	
HPB_CAPS	11.1	-	CAPS, Nafion
HPB_CLD770AL_1	3.7	90%	
HPB_CLD770AL_2	40.5 (should be 100%, prob. defective valve)	-	Au-Converter
HPB_CLD770AL_3	9.0	50%	
IAGOS	2.7		
ICAD	0.0	-	DOAS
IPR_CAPS	0.7	-	CAPS, Nafion
IPR_TE42iTL	100.0	-	Mo, without Nafion
IPR_TE42iTL	0*	-	Mo, with Nafion
ISAC	-1.1		
MD_42itl	90.0	-	Mo
MD_AS32M	0.4	-	CAPS, Nafion
SIRTA	7.6*		Nafion
TROPOS	9.4		

* 30-50% of HONO appear as NO and 0-10% as NO_2 by the NAFION dryer

Results

- Participant calibrations deviate up to 10% from reference in dry conditions (Figure 1).
- A substantial part showed changes in sensitivity larger than the DQO.
- Dilution systems are more critical in calibration than standard gases.
- Instruments based on the same technique show differences.
- HONO causes significant interferences (Figure 3 and table) for all instruments (without Nafion) but the ICAD. Either NO or NO_2 channel is affected to a larger extent depending on the presence of a Nafion dryer.
- Nafion dryers convert HONO to NO.
- HONO interferences increase with higher NO_2-to-NO converter efficiencies.
- Molybdenum converters show unexpected water vapour artefacts for large artificial temporal gradients of humidity.
- The data quality objectives for NO and NO_2 are not met at current state.

Outlook

- Achieving data quality objectives requires further development of the measurement systems and QA/QC.
- Establishment of a round robin system = a standard cylinder spiked with CO_2 and a Picarro to control dilution.
- Further analyses to identify critical components.
- Potential night time offsets of NO caused by HONO will need to be taken into account.
- Improve Measurement Guidelines (D 3.17).

(1)Meteorological Observatory Hohenpeissenberg (HPB),
(2)Czech Hydrometeorological Institute (CHMI), (3)Institute for Atmospheric Science and Climatology (ISAC),
(4)Finnish Meteorological Institute (FMI), (5)Forschungszentrum Jülich GmbH (IAGOS),
(6)Institute of Environmental Physics Heidelberg (IUP-HD), (7)Joint Research Center of the European Commission (IPR), (8)IMT Lille-Douai (MD),
(9)Laboratoire des Sciences du Climat et de l'Environnement (SIRTA), (10)Leibniz-Institute for Tropospheric Research (TROPOS), (11) Forschungszentrum Jülich GmbH (FZJ)

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 654109.

Meteorologisches Observatorium Hohenpeißenberg
Deutscher Wetterdienst
Albin-Schwaiger- Weg 10
82383 Hohenpeißenberg

Robert.Holla@dwd.de

Bundesministerium für Verkehr, Bau und Stadtentwicklung