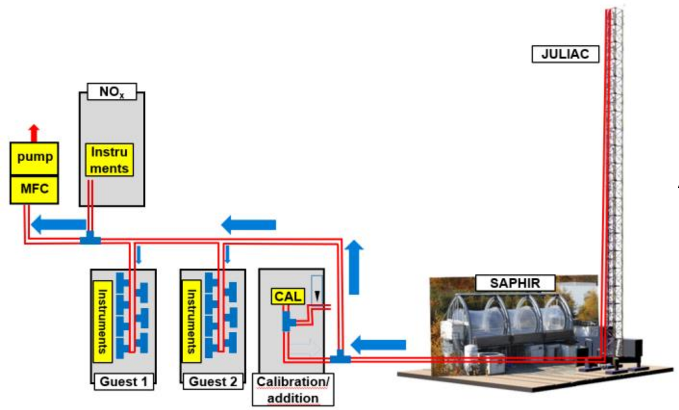
ACTRIS Intercomparison Campaign for Nitrogen Oxides (NO_x) at Research Centre Jülich – JUNOx23

Max Gerrit Adam, Robert Wegener, Franz Rohrer, Benjamin Winter, Lukas Kesper



ACTRIS central calibration facility, CiGas
Research Centre Jülich, FZJN

ACTRIS Intercomparison for Nitrogen Oxides (NO_x), JUNOx23

- **Aim:** (i) To intercompare state-of-the-art instruments for NO_x measurements and investigate potential interferences through experiments under identical conditions

  (ii) To train ACTRIS station members on measurement guidelines and calibration procedures
- **Location:** IEK-8 at Forschungszentrum Jülich, Germany, with SAPHIR atmospheric simulation chamber and JULIAC tower part of the setup
- **Measurement techniques:** Chemiluminescence detection (CLD), Cavity-attenuated phase shift (CAPS), Iterative cavity-enhanced differential optical absorption spectroscopy (ICAD), Tunable Diode quantum cascade laser (TDQCL), Long Path Absorption Photometer (LOPAP), Photoacoustic sensor (PAS), Cavity-Enhanced Absorption Spectroscopy (CEAS), Cavity Ringdown Spectroscopy (CRDS)
- **Experiments:** water vapor, O_3, HONO, CHOCHO, HCHO, alkylnitrites/-nitrates
- **Time Period:** set-up 12-16 June 2023; experimental 19-30 June 2023

Overview of groups and instrumentation

Group	Instruments	Converter
Airyx GmbH, Germany	Airyx ICAD-NOx-200D	GPT: NO to NO_2/NO_x
BAST, Germany	Photoacoustic sensor (PAS)	-
Univ. of Cork, Ireland	Custom-built CEAS/CRDS	-
CMN, Monte Cimone, Italy	Teledyne CLD T200UP	BLC (100%)
CMN, Monte Cimone, Italy	Thermo Scientific CLD 42iTL	BLC (67%)
DWD, Germany	EcoPhysics CLD 770 AL	Heated Gold surface&CO
DWD, Germany	EcoPhysics CLD 770 AL	PLC
DWD_nCLD, Germany	Ecophysics nCLD899	BLC
DWD_CAPS1, Germany	Aerodyne CAPS	-
DWD_CAPS2, Germany	Teledyne CAPS	-
FRA, Goethe Univ. Frankfurt, Germany	Ecophysics CLD 780	Installation after the campaign
HEL, Helios, France	Ecophysics CLD 780 TR	-
HEL, Helios, France	Thermo Fisher CLD 42i	Molybdenum
HEL, Helios, France	Environnement S.A AS32M CAPS	-
HEL, Helios, France	Aerodyne CAPS	-
IAS, Univ. of Iasi, Romania	ECOTECH CLD EC9841	Molybdenum
IMT, France	Aerodyne CAPS	-
IMT, France	Teledyne CLD T200UP	BLC
LEI, Univ. of Leicester/Birmingham, UK	Teledyne T500U CAPS	-
NOT, Nottingham, UK	Airyx ICAD 200-UV1-L	GPT: NO to NO_2/NO_x
QUA, Univ. of Wuppertal, Germany	LOPAP	-
QUA, Univ. of Wuppertal, Germany	ECO Physics CLD 899 Y	Molybdenum+PLC
TRO, TROPOS, Germany	Teledyne CLD T200UP (2x)	BLC
TRO, TROPOS, Germany	Thermo 42i CLD	BLC
TRO, TROPOS, Germany	CAPS	BLC
YOR, Univ. of York, Germany	Airyx ICAD	GPT: NO to NO_2/NO_x

Measurement by chemiluminescence (CLD)

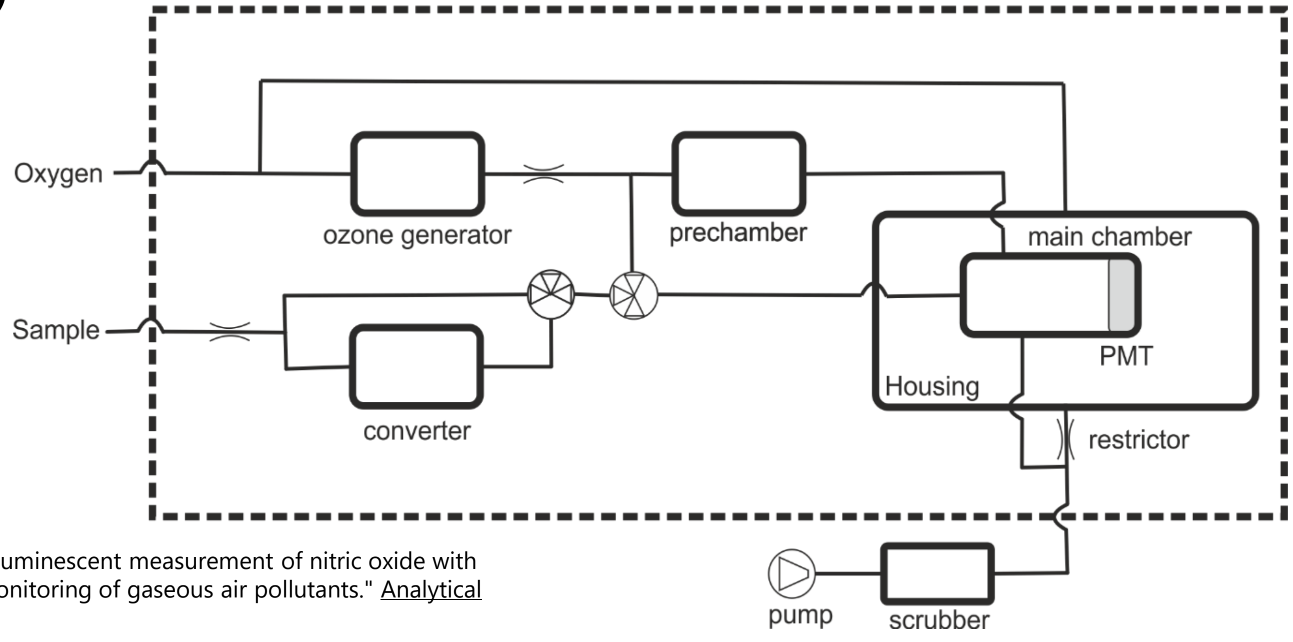
$NO + O_3 \rightarrow NO_2 + O_2$

$NO + O_3 \rightarrow NO_2^* + O_2$

$NO_2^* + M \rightarrow NO_2$, $M = N_2, O_2, H_2O, Ar$

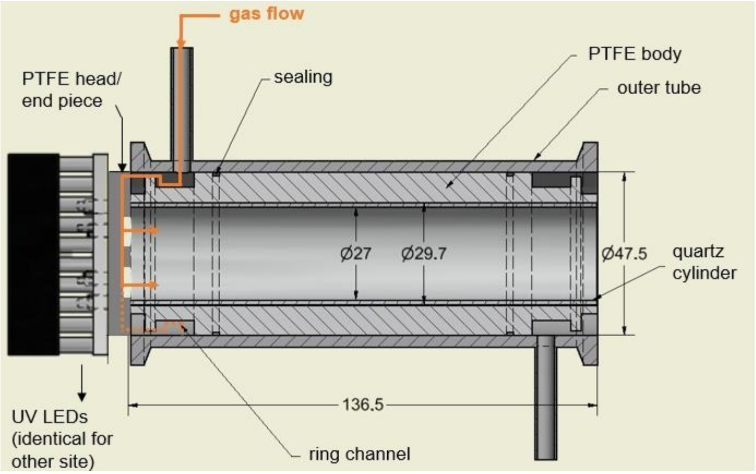
$NO_2^* \rightarrow NO_2 + h \cdot \nu$

$(590 \leq \lambda \leq 3000 \text{ nm})$



Fontijn, A., et al. (1970). "Homogeneous chemiluminescent measurement of nitric oxide with ozone. Implications for continuous selective monitoring of gaseous air pollutants." Analytical Chemistry **42**(6): 575-579.

Measurement by chemiluminescence

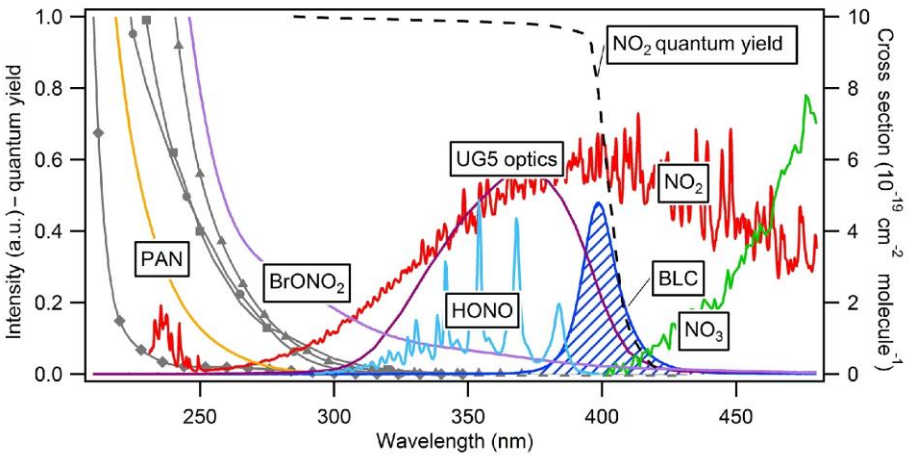


Nussbaumer, C. M., et al. (2021). "Modification of a conventional photolytic converter for improving aircraft measurements of NO2 via chemiluminescence." Atmos. Meas. Tech. **14**(10): 6759-6776.

Conversion to NO by Photolysis

$NO_2 + h\cdot\nu \rightarrow NO + O^3(P)$

Xenon lamps or
UV emitting diodes ("blue light converters, BLC")
→ *Photolytic converters recommended in ACTRIS*



Reed, C., et al. (2016). "Interferences in photolytic NO2 measurements: explanation for an apparent missing oxidant?" Atmos. Chem. Phys. **16**(7): 4707-4724.

- Spectral band width should be small
- No overlap with PAN
- But some overlap with HONO and $BrONO_2$

Spectroscopic techniques

Cavity attenuated phase shift spectroscopy (CAPS) — Kebabian et al., 2008. , *Environmental Science & Technology*, 42: 6040-45.

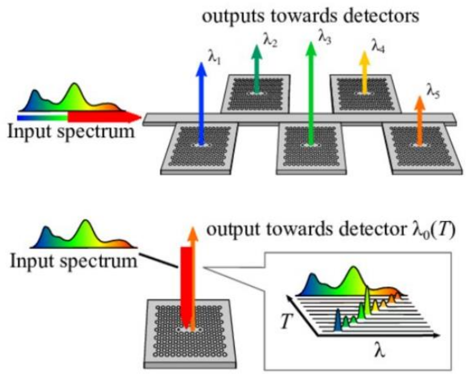
Quantum Cascade Laser (QCL) — Tuzson et al., 2013. *Atmospheric Measurement Techniques*, 6: 927-36.

Iterative cavity-enhanced DOAS (ICAD) — Horbanski et al., 2019. Atmospheric Measurement Techniques, 12: 3365-81.

Long Path Absorption Photometer (LOPAP) — Villena et al., 2011. Atmospheric Measurement Techniques, 4: 1663-76.

Cavity-Enhanced Absorption Spectroscopy (CEAS) — Gherman et al., 2008. *Environmental Science & Technology*, 42: 890-95.

- Enable direct NO_2 measurements
- Conversion of NO into NO_2 needed
- Ozone inlet correction still needed
- Also, humidity may cause problems

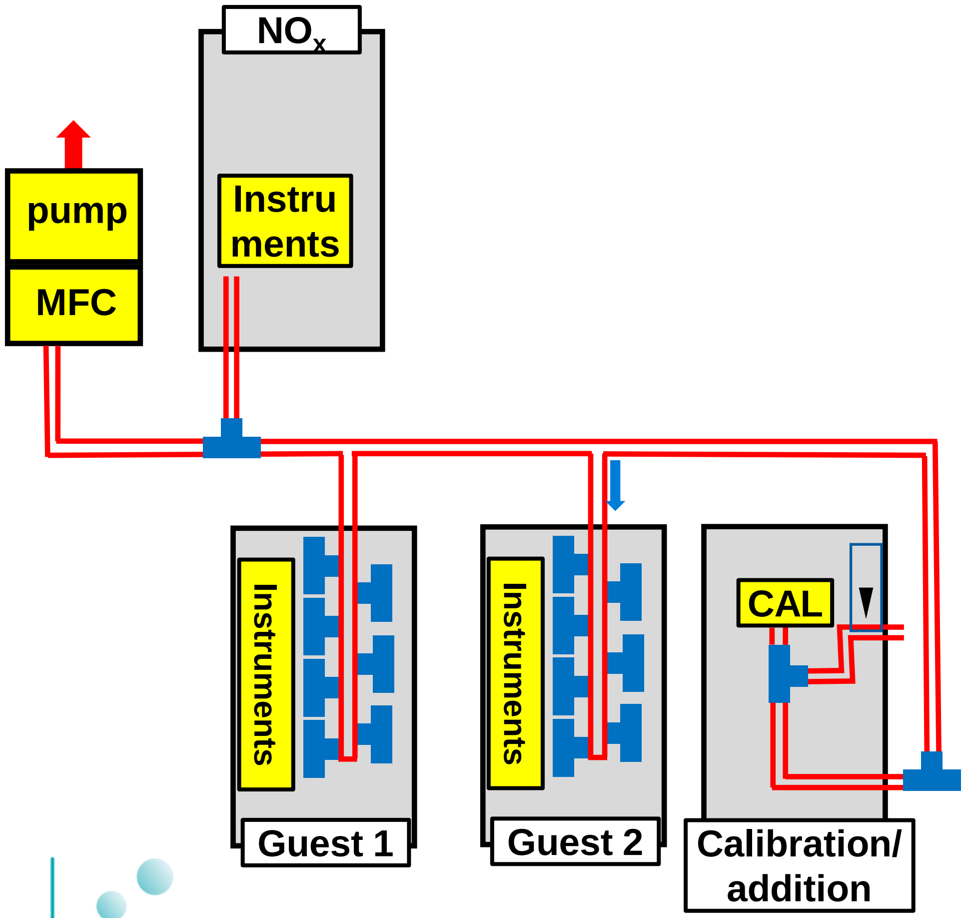


Source: Liapis et al., 2015. Applied Physics Letters, 108: 021105.

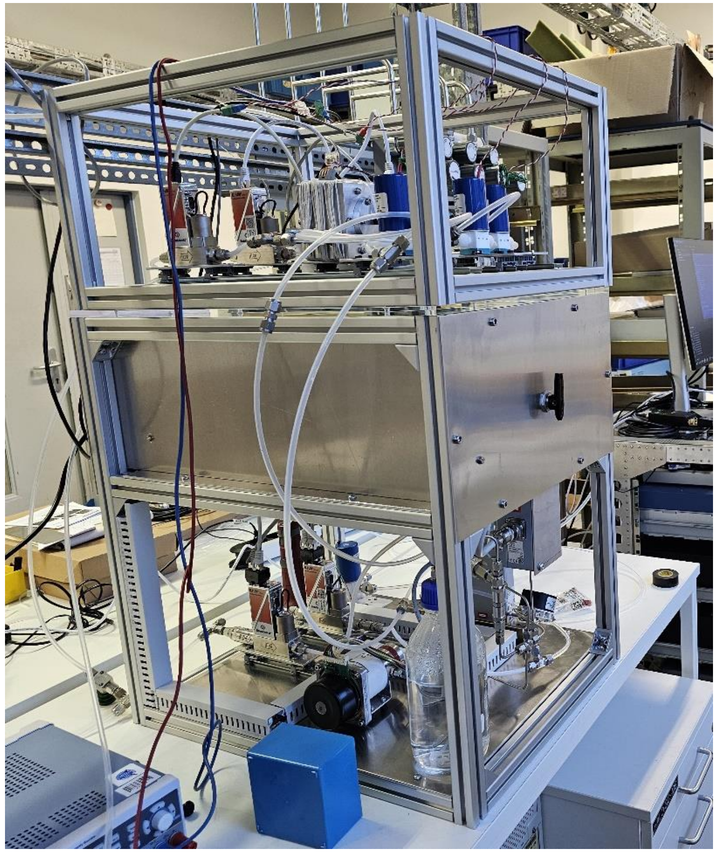
ACTRIS Intercomparison for Nitrogen Oxides (NO_x)

SAPHIR + JULIAC setup

JUNOx23 Setup and other data



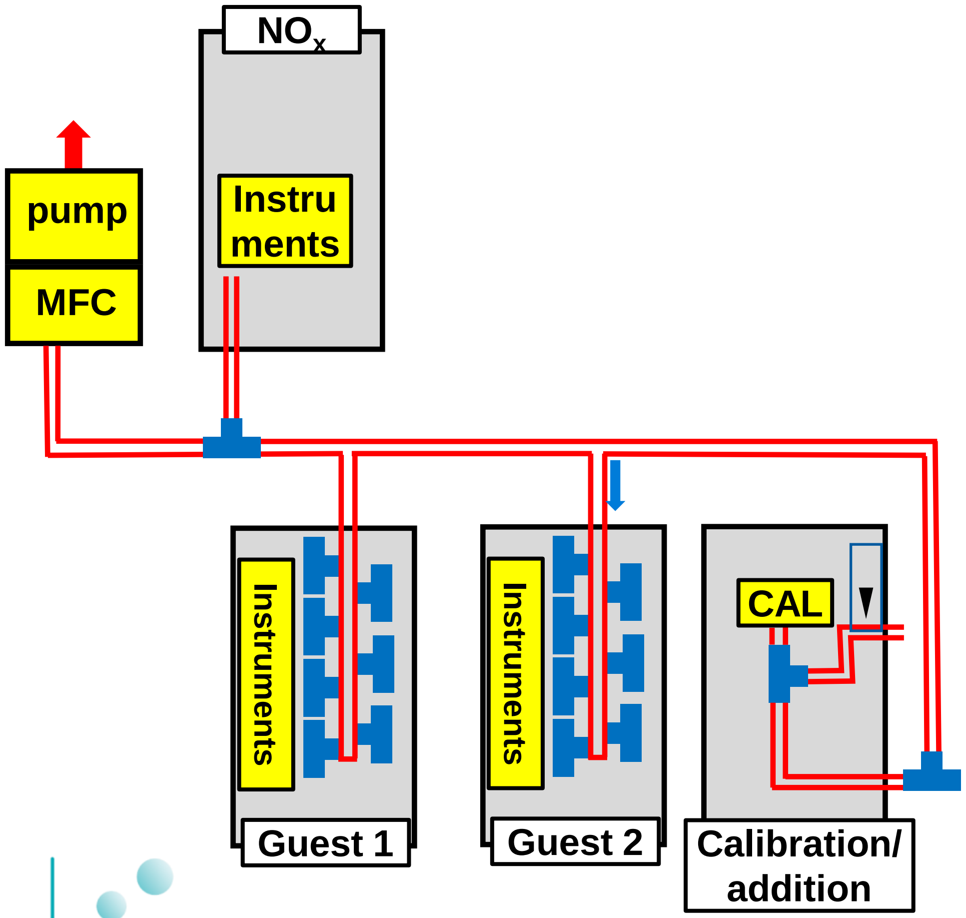
CEM system for addition of gases



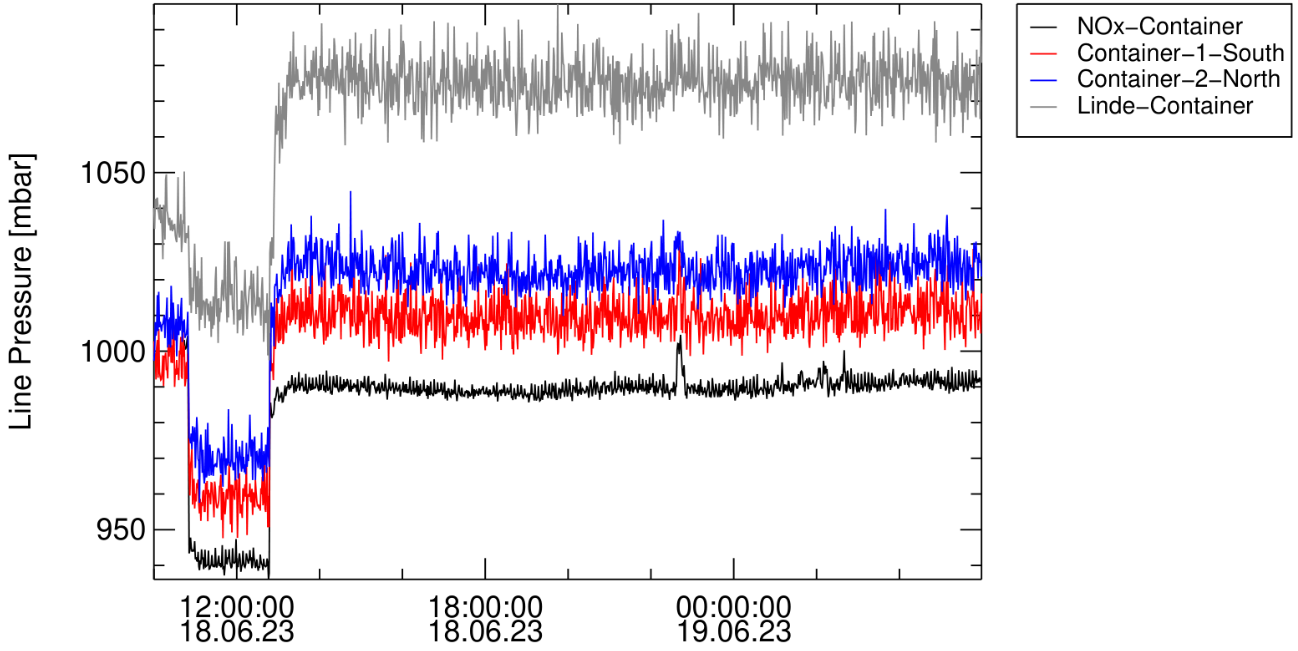
Custom-built Controlled Evaporation Mixing (CEM) system which can be also used for precise addition of experimental gases

ACTRIS CiGas

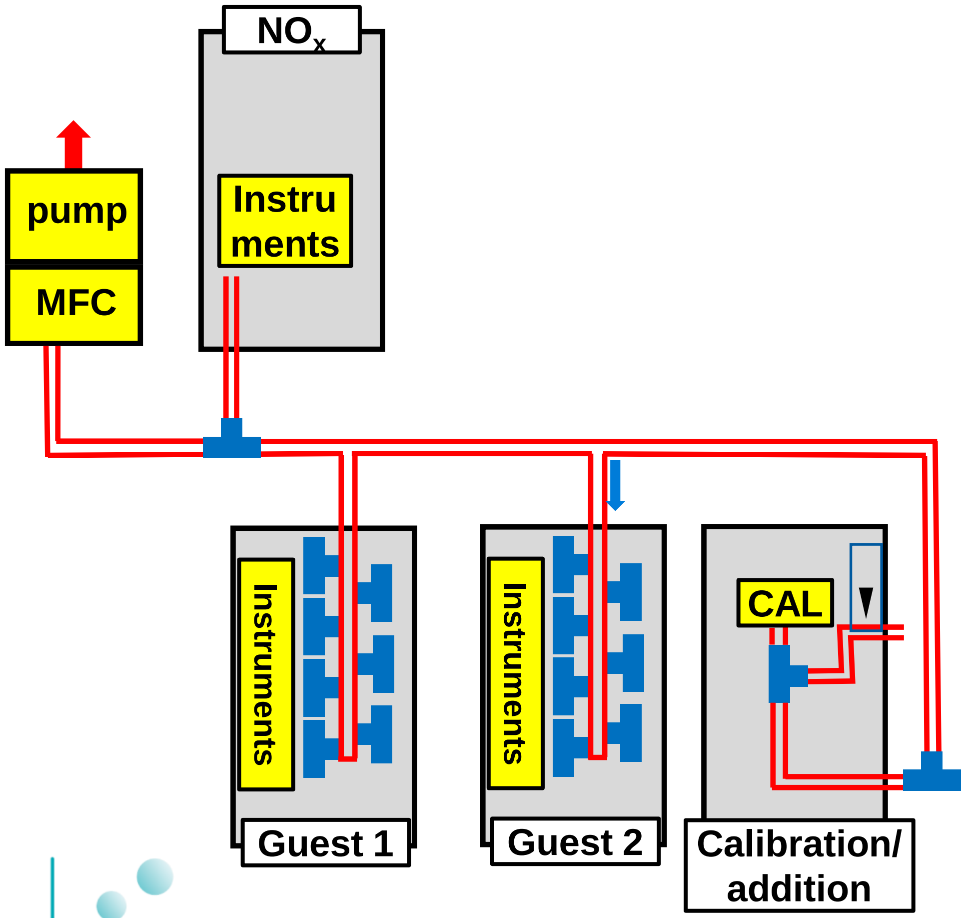
JUNOx23 Setup and other data



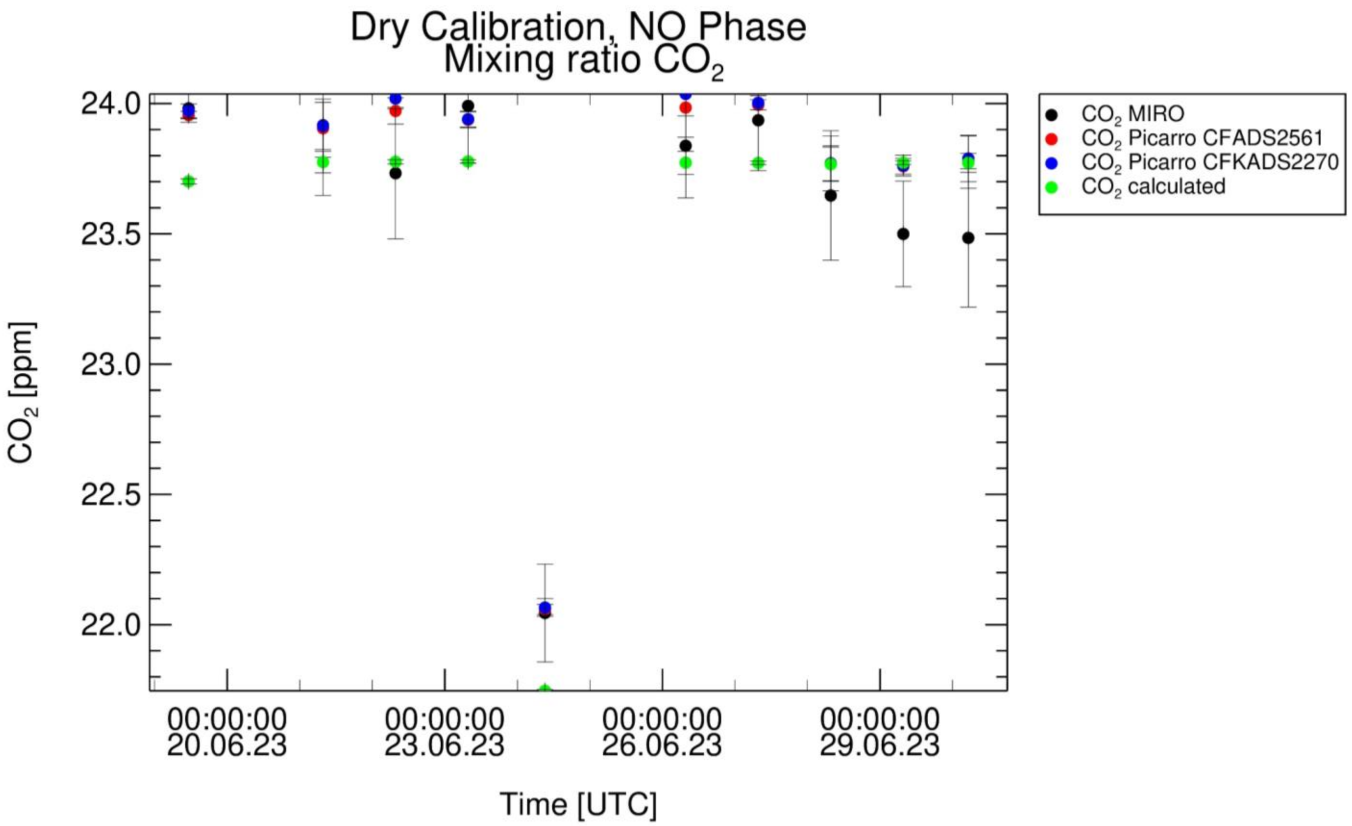
Monitoring of pressure across the sample line



JUNOx23 Setup and other data



CO_2 values from addition of NO reference standard



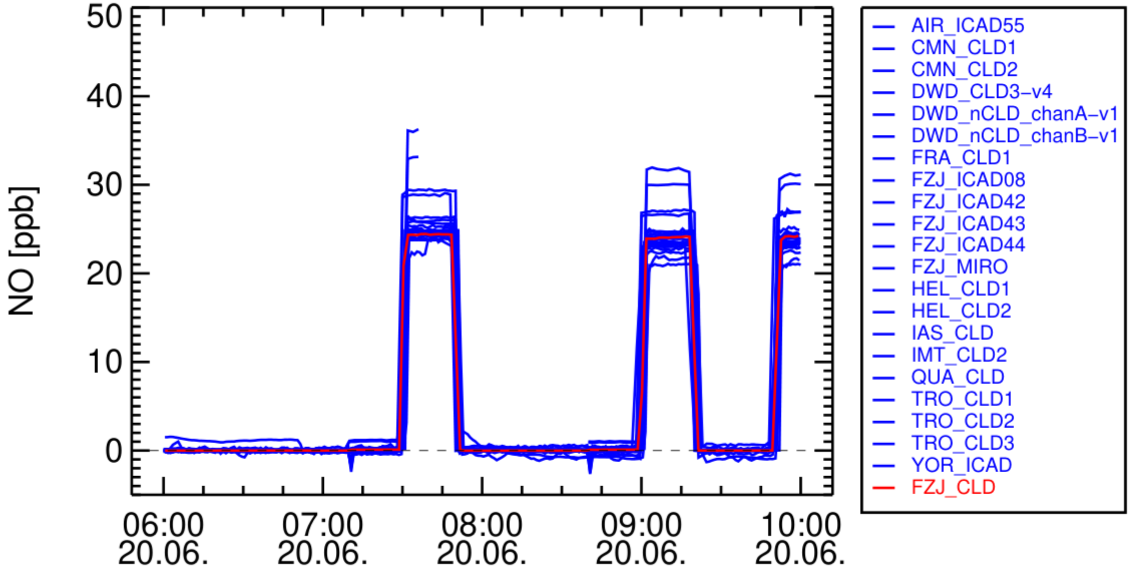
- CO_2 values agree within 1% of the values calculated from the flow controllers
- Further parameters measured H_2O, O_3

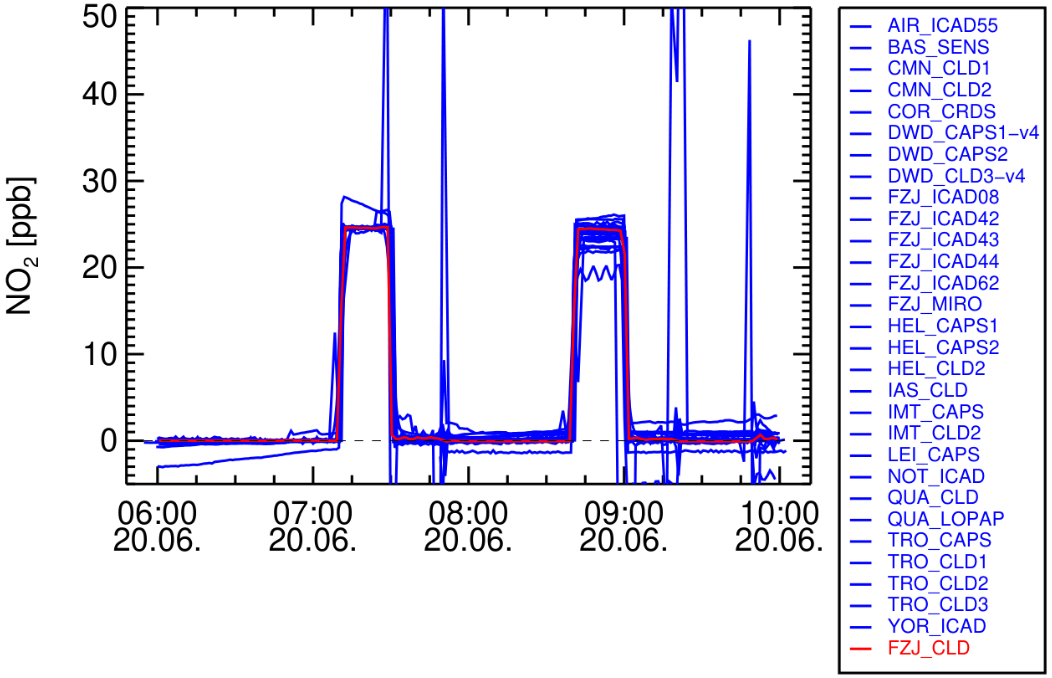
Calibration for NO_x

Sequence during JUNOx23

- Daily calibration dry / humid
- NO from reference gas standard (NPL)
- NO_2 is produced from reaction with Ozone, no NPL standard available

Synthetic air	O_3	$NO + O_3 = NO_2$	NO
20min	20min	20min	20min





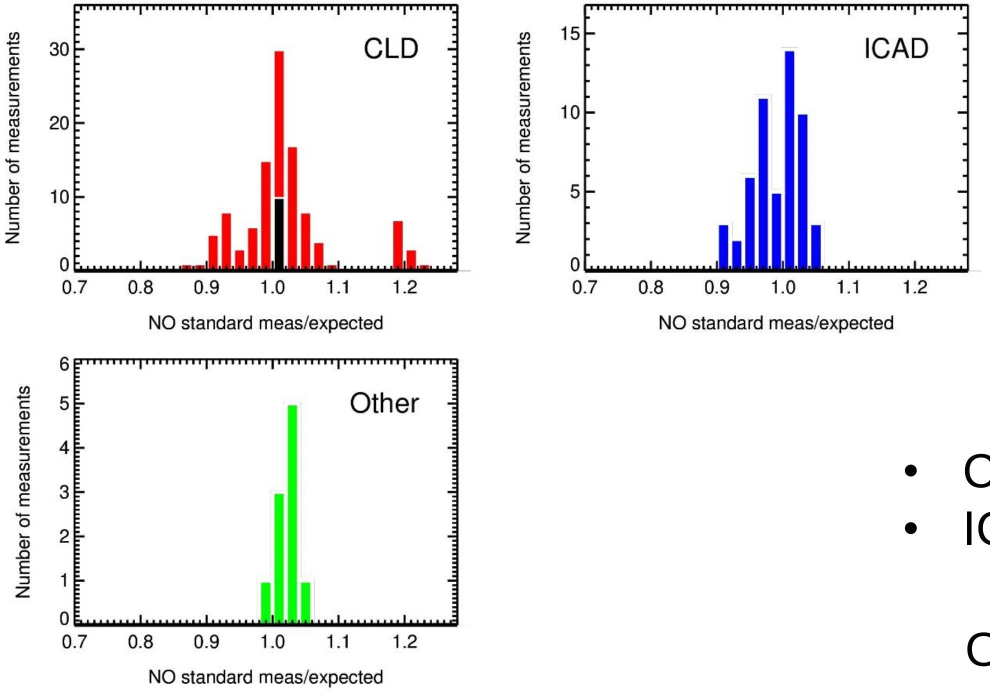
ACTRIS CiGas

Preliminary results

Sensitivities of NO measurements

FZJ CLD standard meas/expected

NO standard meas/expected



FZJ CLD : Mean: 1.0000 ± 0.0000 Median: 1.0000

CLD : Mean: 1.0483 ± 0.1251 Median: 1.0142

ICAD : Mean: 0.9922 ± 0.0377 Median: 1.0012

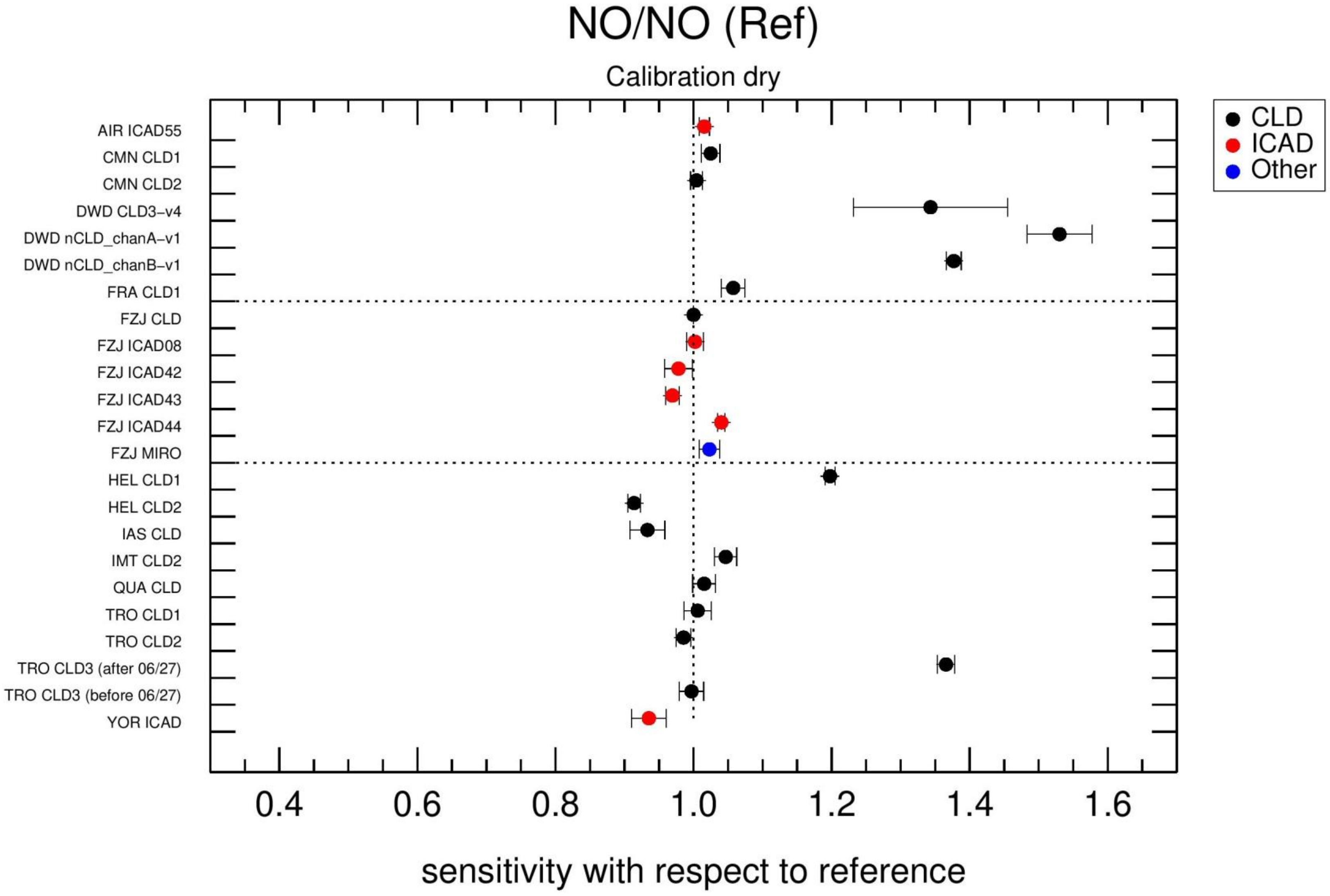
Other : Mean: 1.0243 ± 0.0152 Median: 1.0266

- CLDs due to outlier slightly over 1
- ICADs close to 1

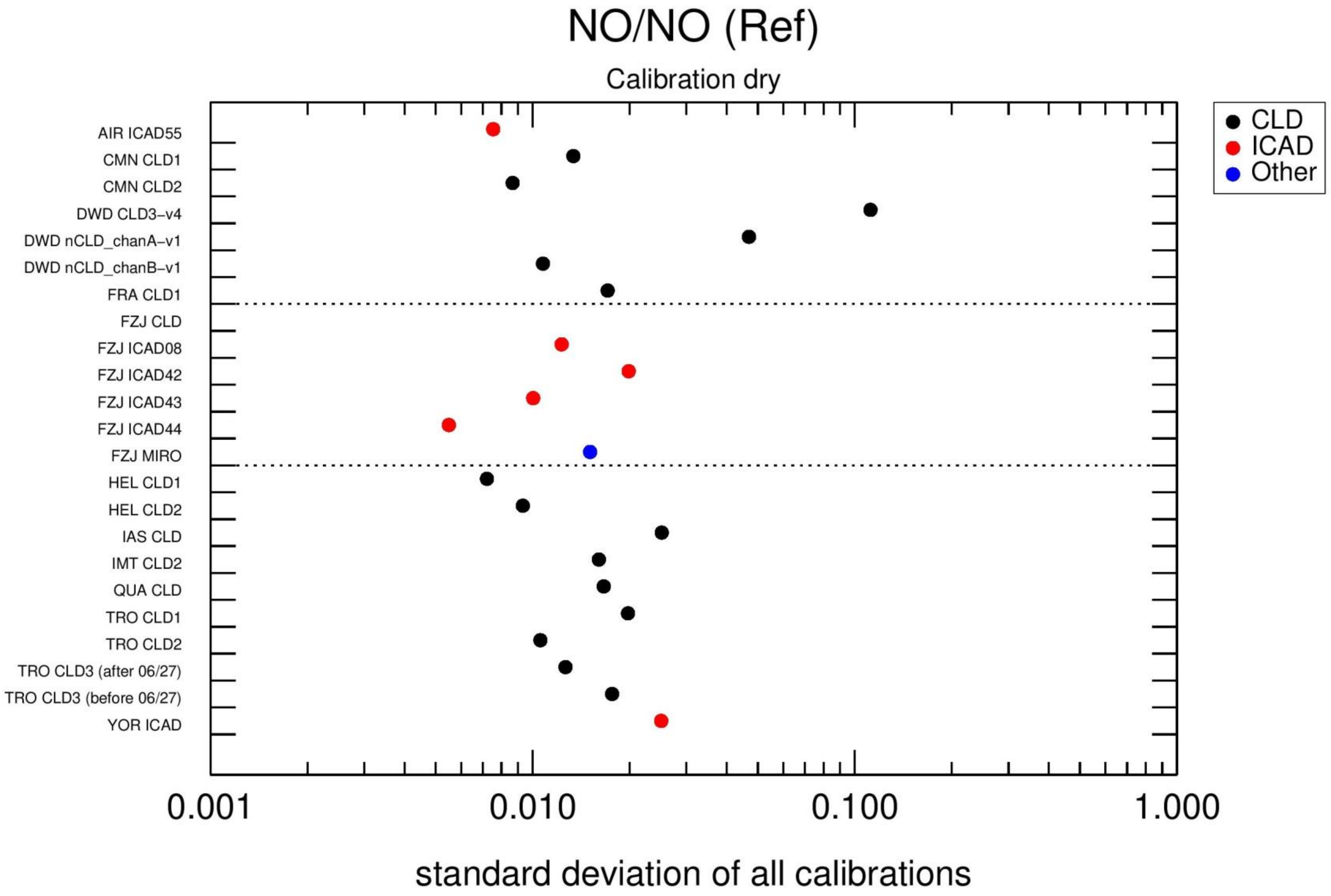
Other: MIRO

ACTRIS CiGas

Sensitivities of NO measurements



Uncertainties of the instruments for NO

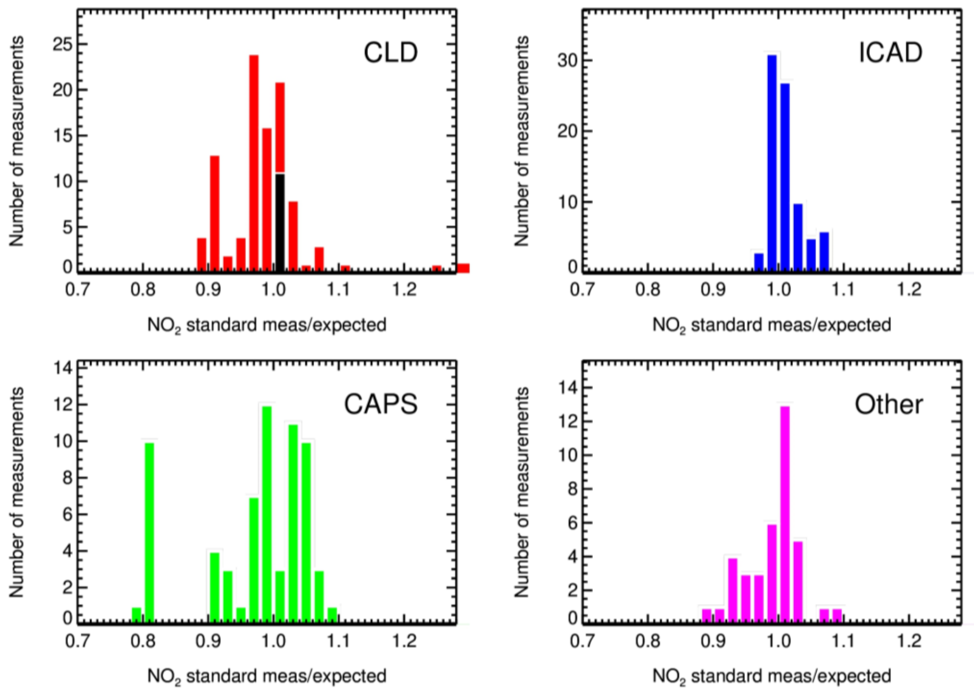


ACTRIS CiGas

Sensitivities of NO_2 measurements

FZJ CLD standard meas/expected

NO_2 standard meas/expected



FZJ CLD : Mean: 1.0000 ± 0.0000 Median: 1.0000

CLD : Mean: 1.0180 ± 0.1298 Median: 0.9846

ICAD : Mean: 1.0103 ± 0.0237 Median: 1.0028

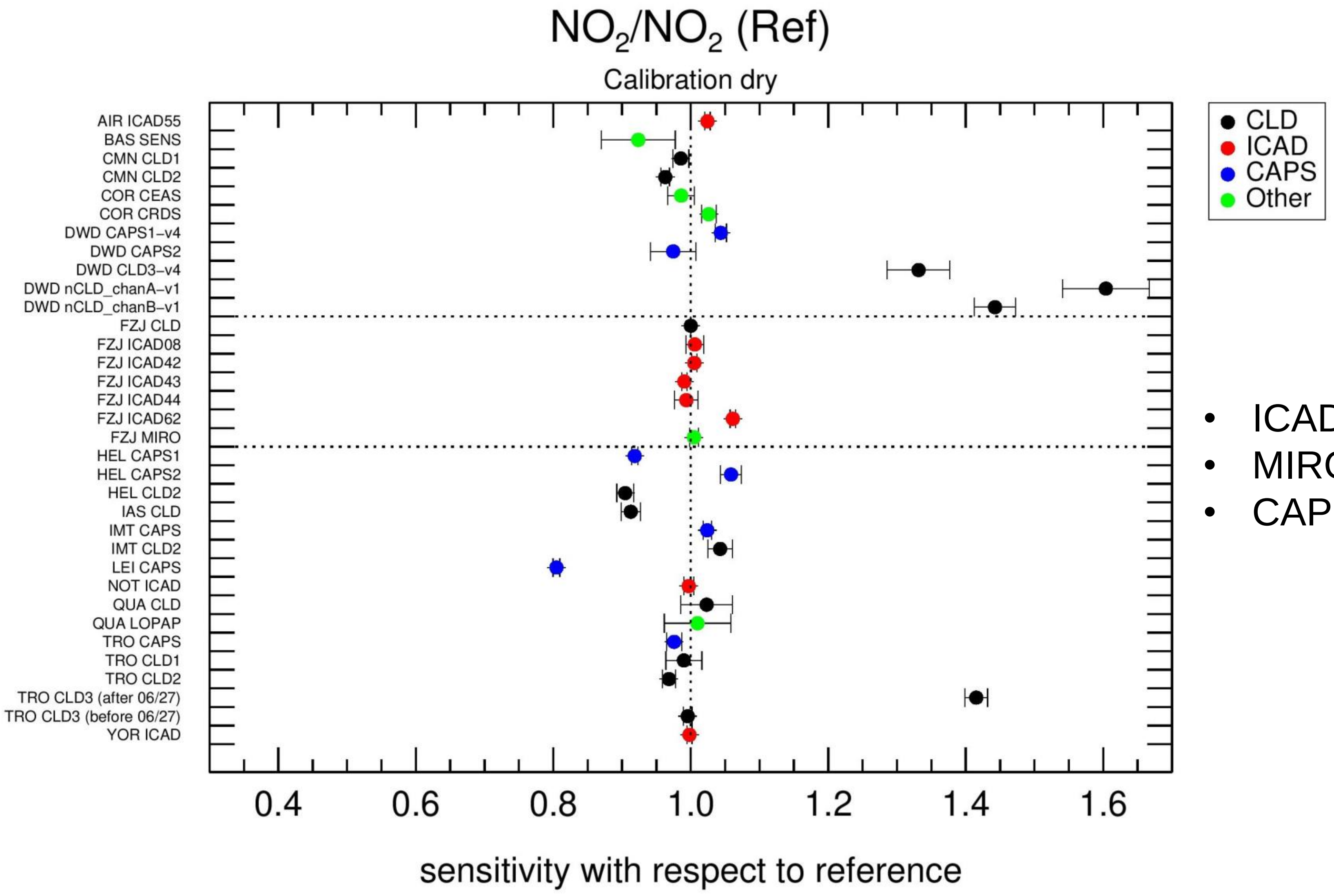
CAPS : Mean: 0.9709 ± 0.0858 Median: 0.9863

Other : Mean: 0.9909 ± 0.0429 Median: 1.0033

Other: LOPAP, CEAS, PAS

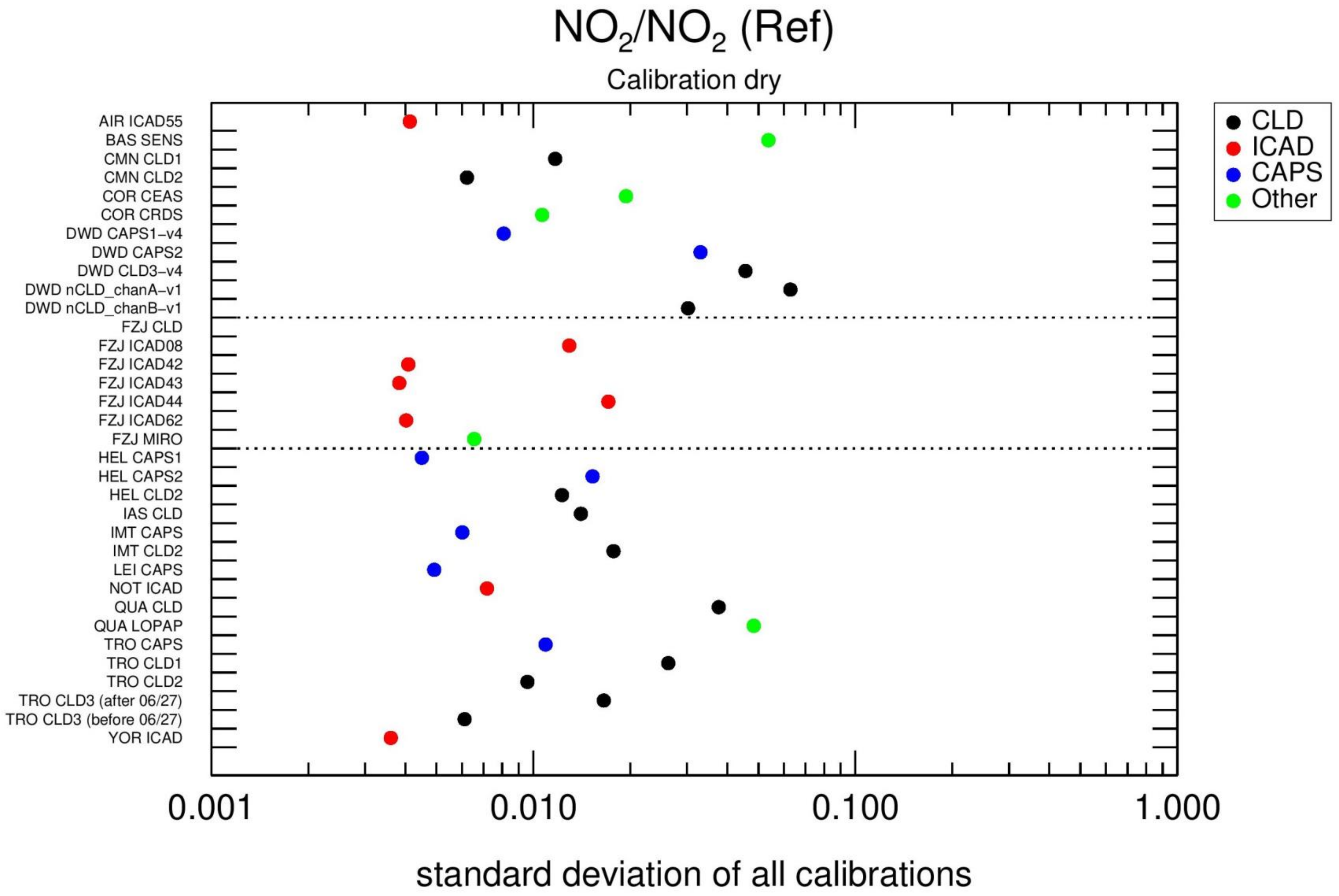
ACTRIS CiGas

Sensitivities of NO_2 measurements



- ICADs for NO_2 close to 1
- MIRO, LOPAP, CEAS are close to 1
- CAPS and CLD show some variation

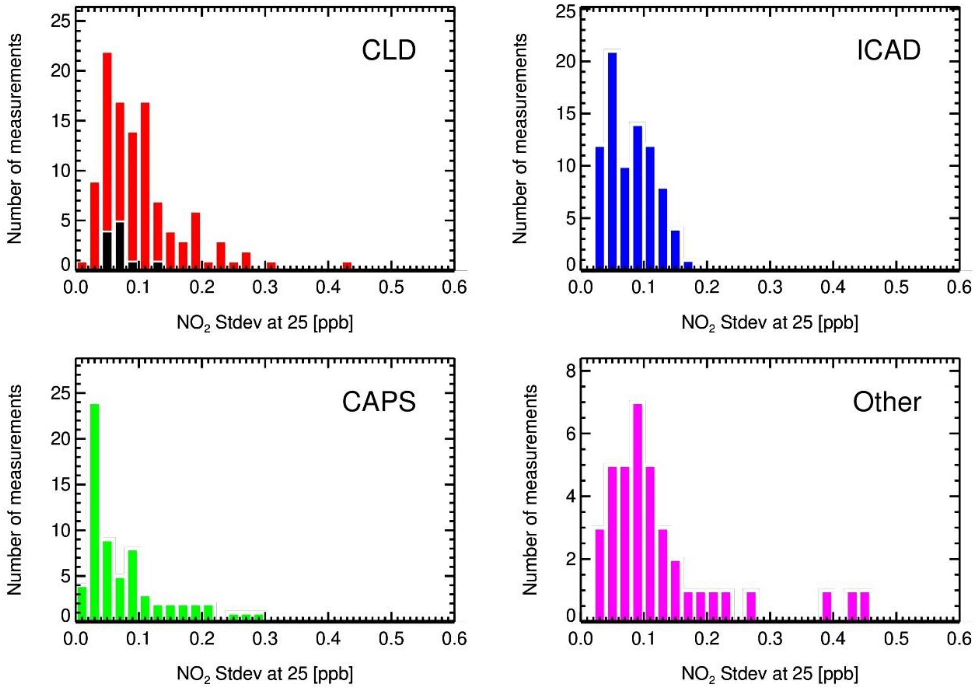
Uncertainties of the instruments for NO_2



Uncertainties of the instruments at 25ppb

FZJ CLD Stdev at 25 [ppb]

NO_2 Stdev at 25 [ppb]



FZJ CLD : Mean: 0.0685 ± 0.0242 Median: 0.0646

CLD : Mean: 0.1064 ± 0.0694 Median: 0.0907

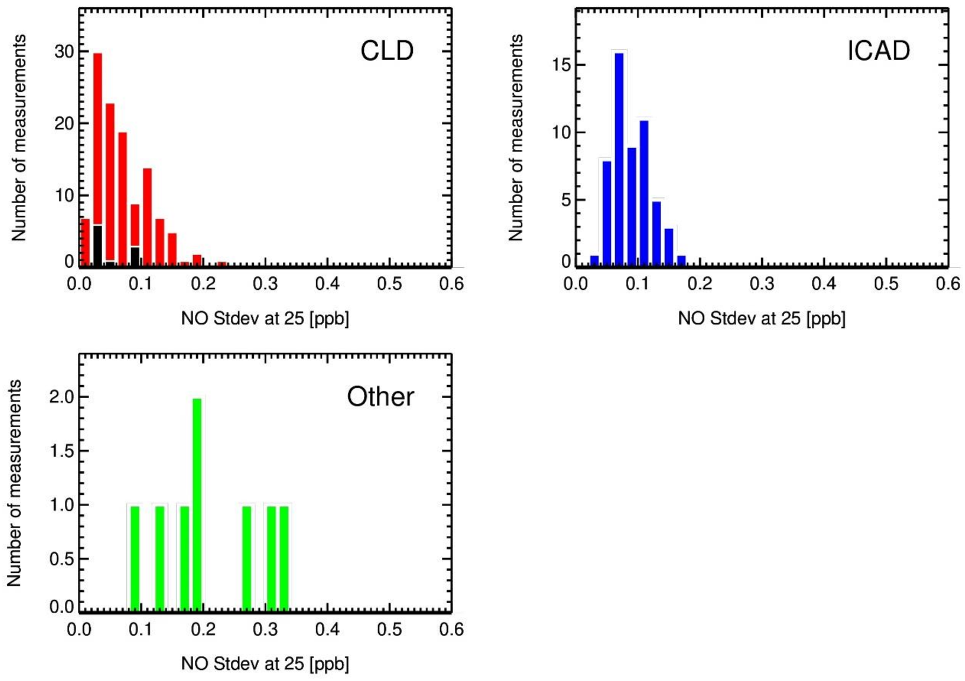
ICAD : Mean: 0.0791 ± 0.0350 Median: 0.0746

CAPS : Mean: 0.0783 ± 0.0658 Median: 0.0459

Other : Mean: 0.1278 ± 0.1028 Median: 0.0988

FZJ CLD Stdev at 25 [ppb]

NO Stdev at 25 [ppb]



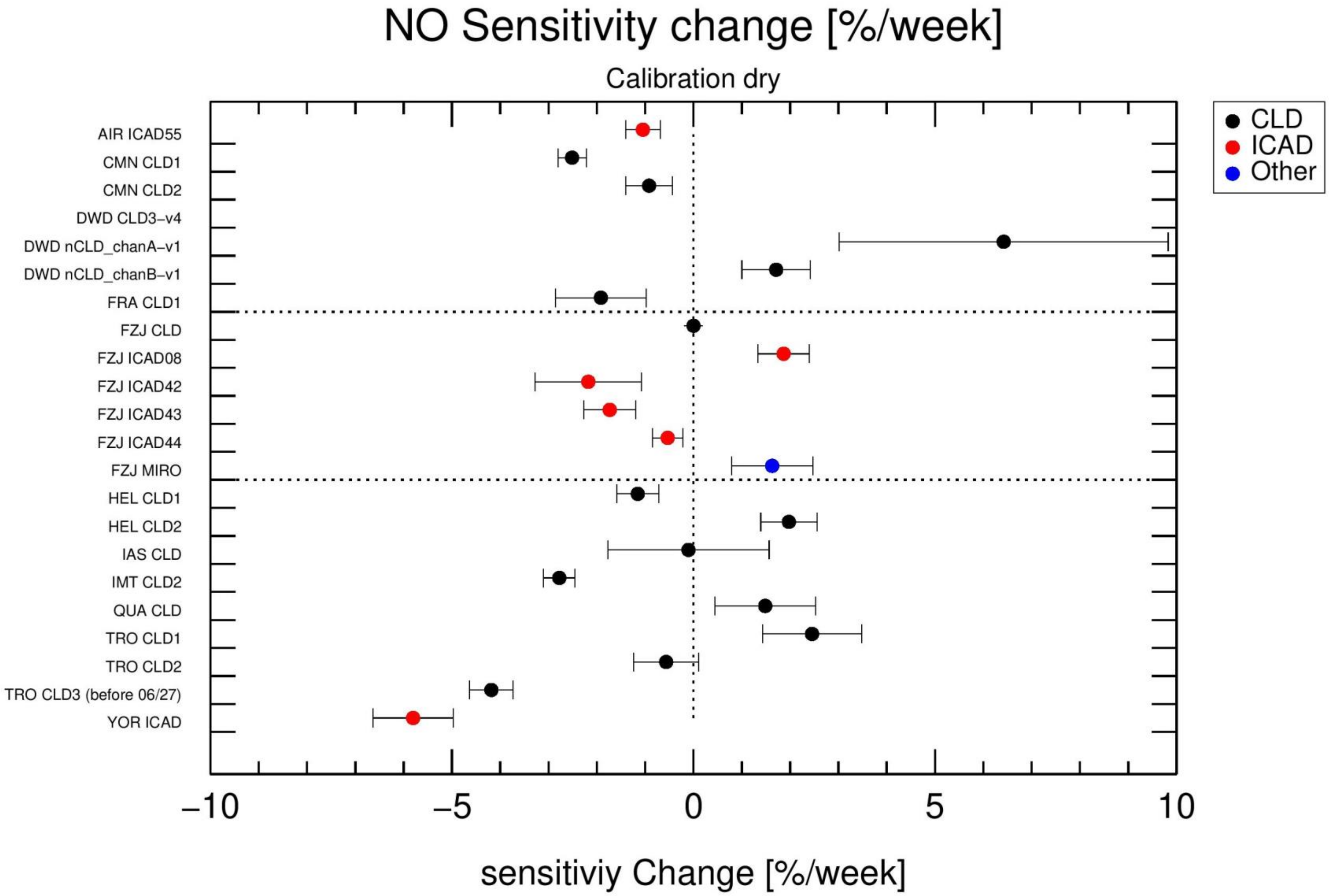
FZJ CLD : Mean: 0.0508 ± 0.0280 Median: 0.0384

CLD : Mean: 0.1152 ± 0.4576 Median: 0.0640

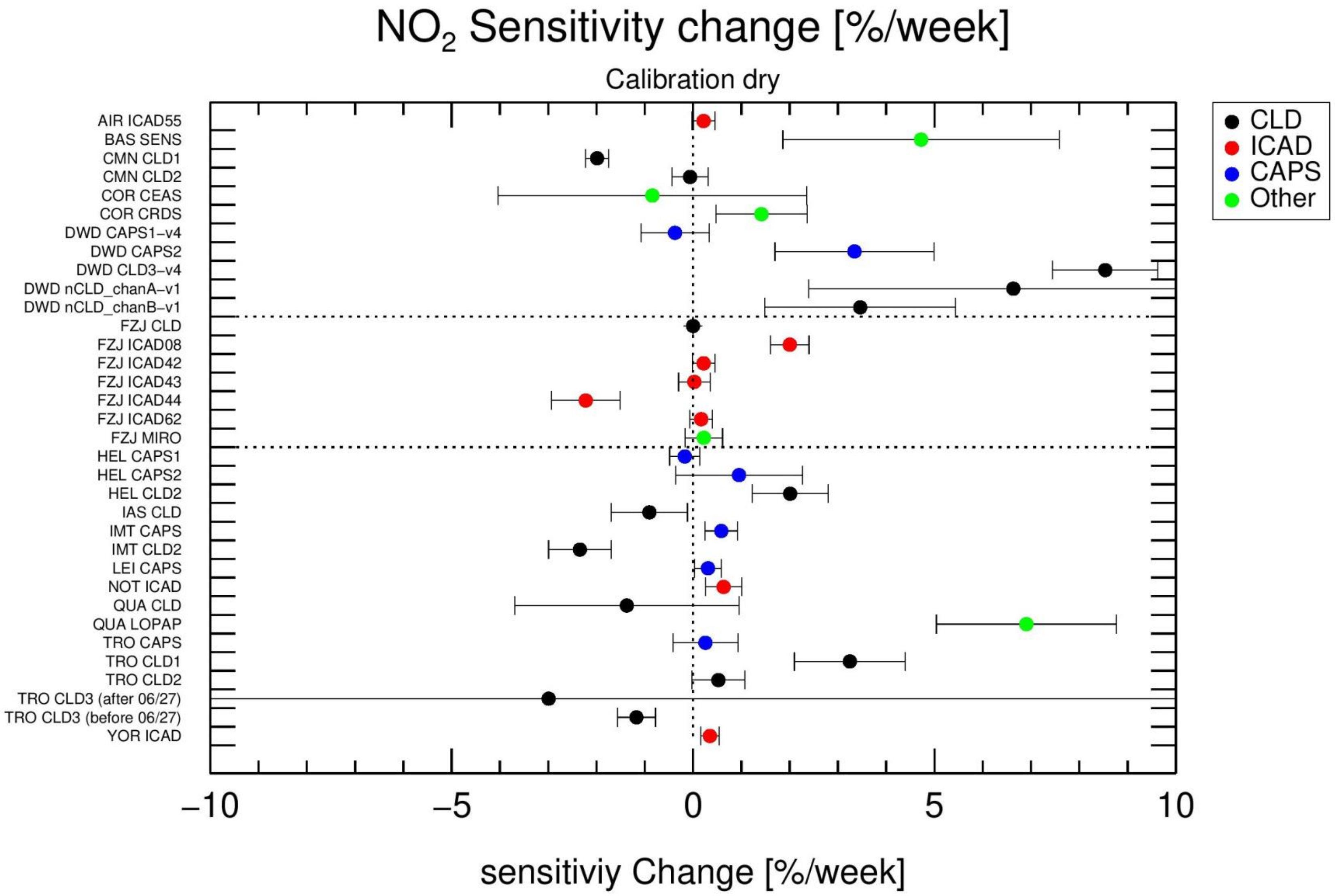
ICAD : Mean: 0.0902 ± 0.0308 Median: 0.0896

Other : Mean: 0.3273 ± 0.2769 Median: 0.2758

Trends in sensitivity of NO observations



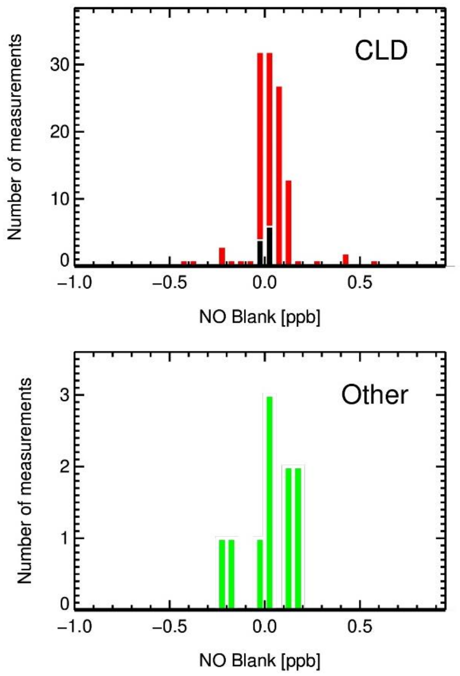
Trends in sensitivity of NO_2 observations



Measurements at zero

FZJ CLD Blank [ppb]

NO Blank [ppb]



FZJ CLD : Mean: –0.0014 ± 0.0063 Median: 0.0004

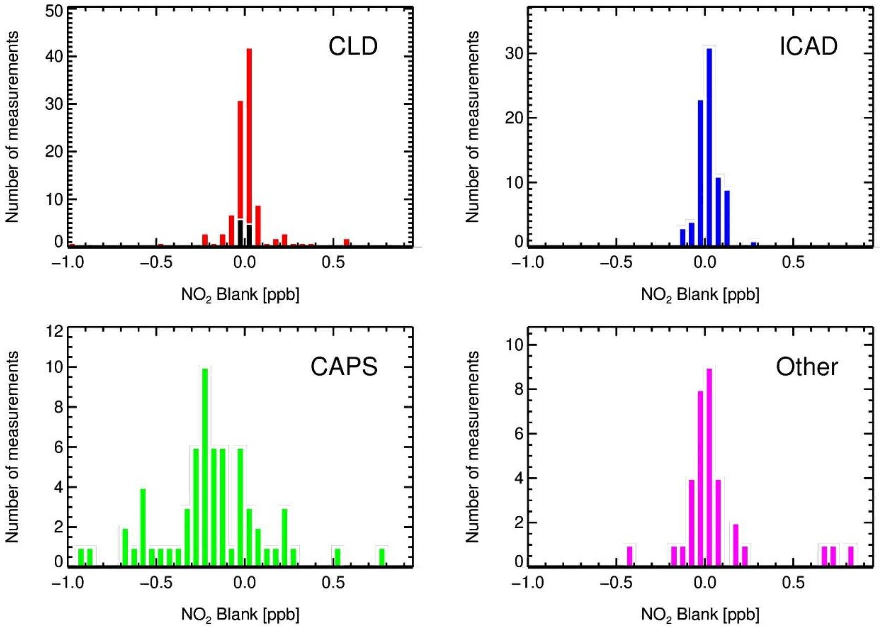
CLD : Mean: 0.0572 ± 0.1909 Median: 0.0442

ICAD : Mean: –0.0182 ± 0.1264 Median: –0.0143

Other : Mean: 0.0185 ± 0.1431 Median: 0.0423

FZJ CLD Blank [ppb]

NO_2 Blank [ppb]



FZJ CLD : Mean: –0.0009 ± 0.0021 Median: –0.0003

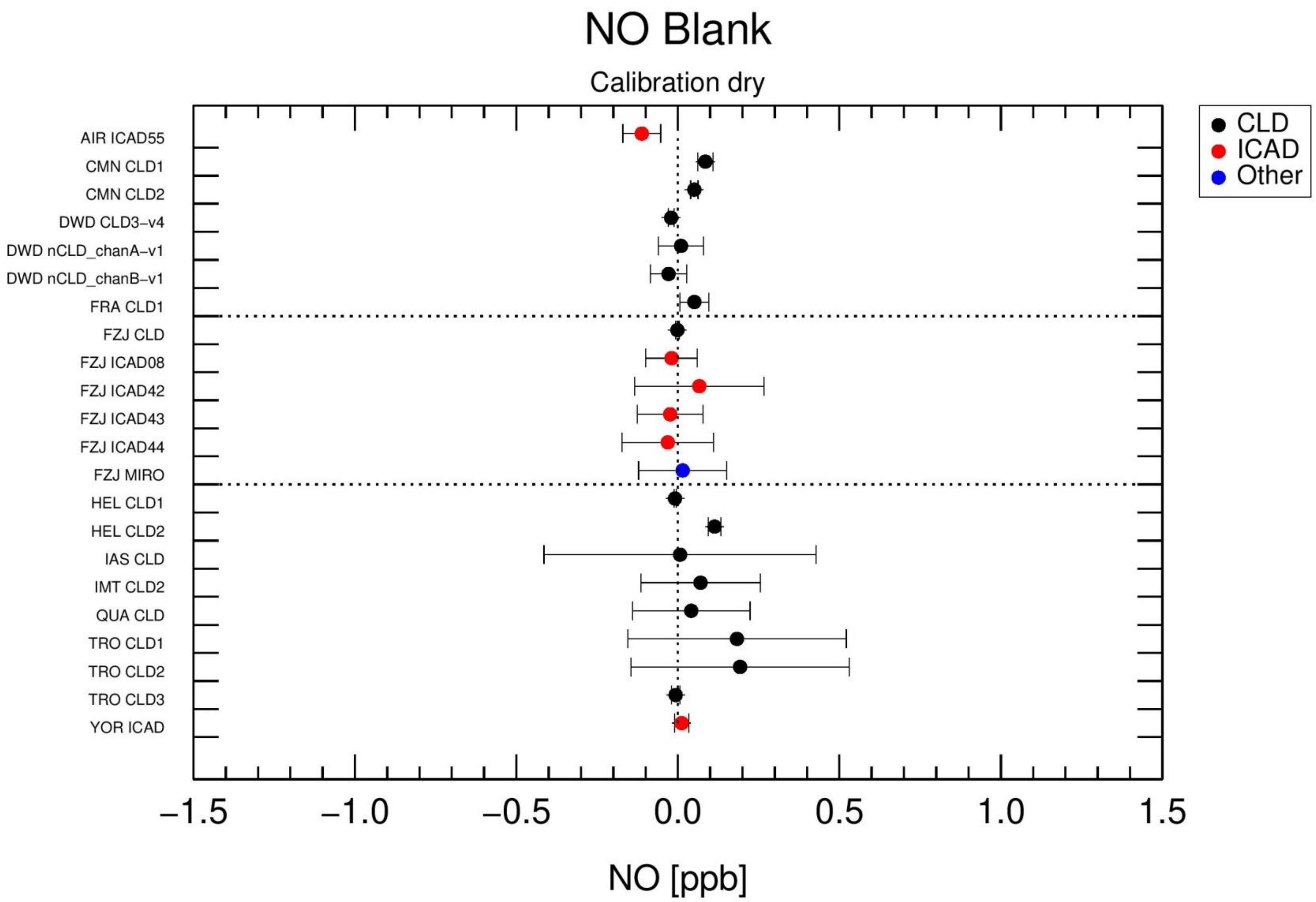
CLD : Mean: 0.0116 ± 0.1656 Median: 0.0113

ICAD : Mean: 0.0226 ± 0.0636 Median: 0.0108

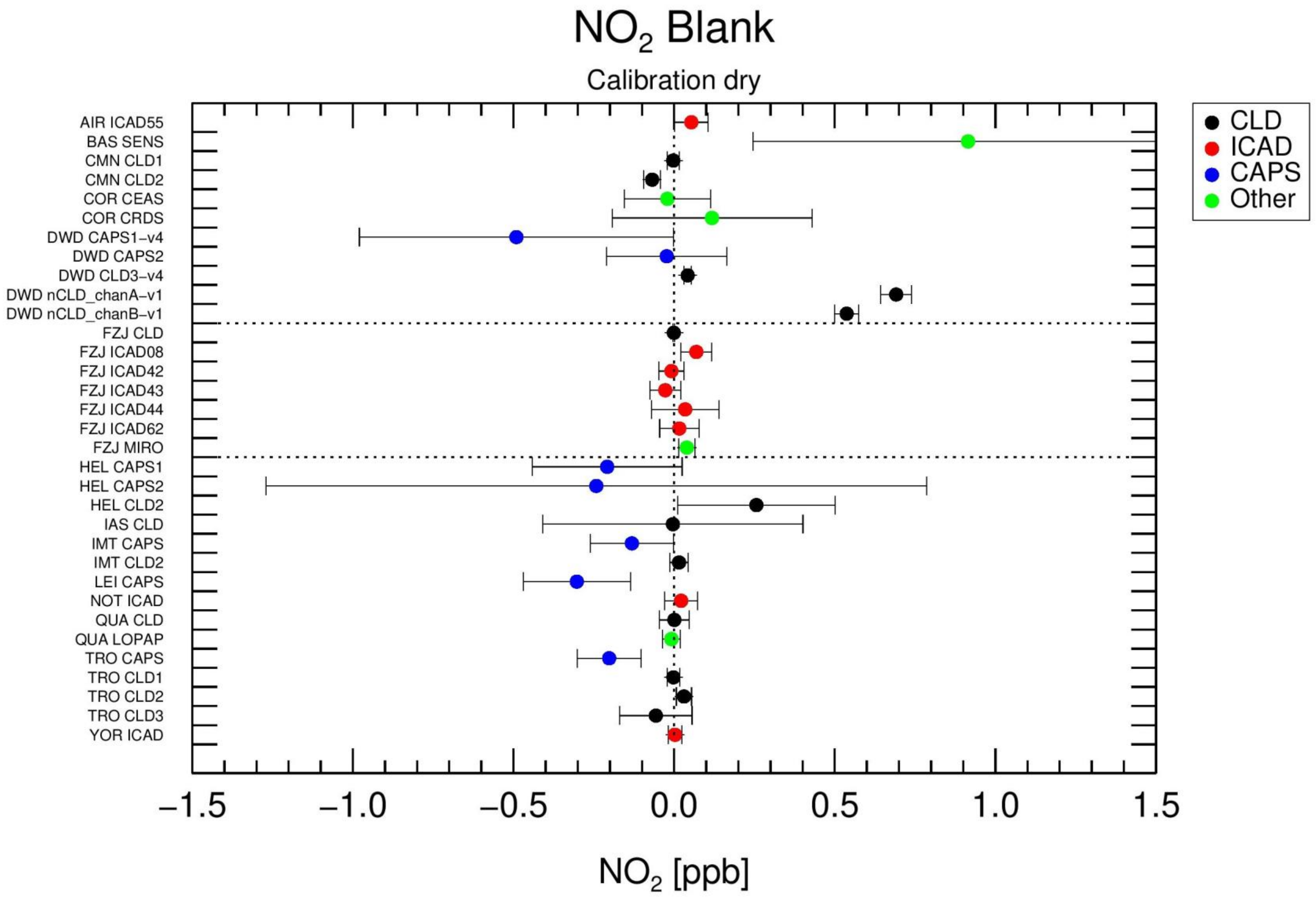
CAPS : Mean: –0.2397 ± 0.4325 Median: –0.2059

Other : Mean: 0.2160 ± 0.5020 Median: 0.0289

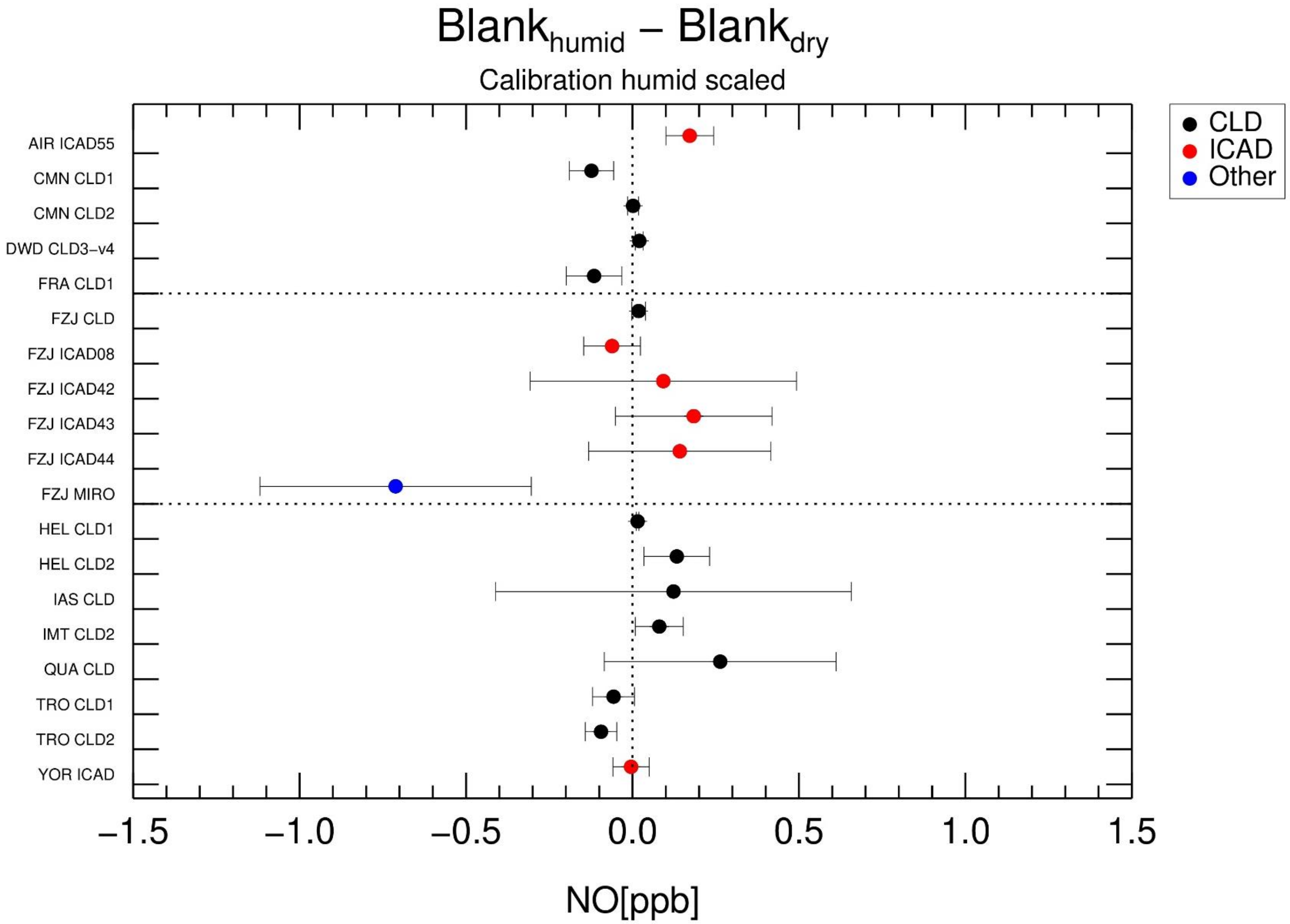
Measurements at zero



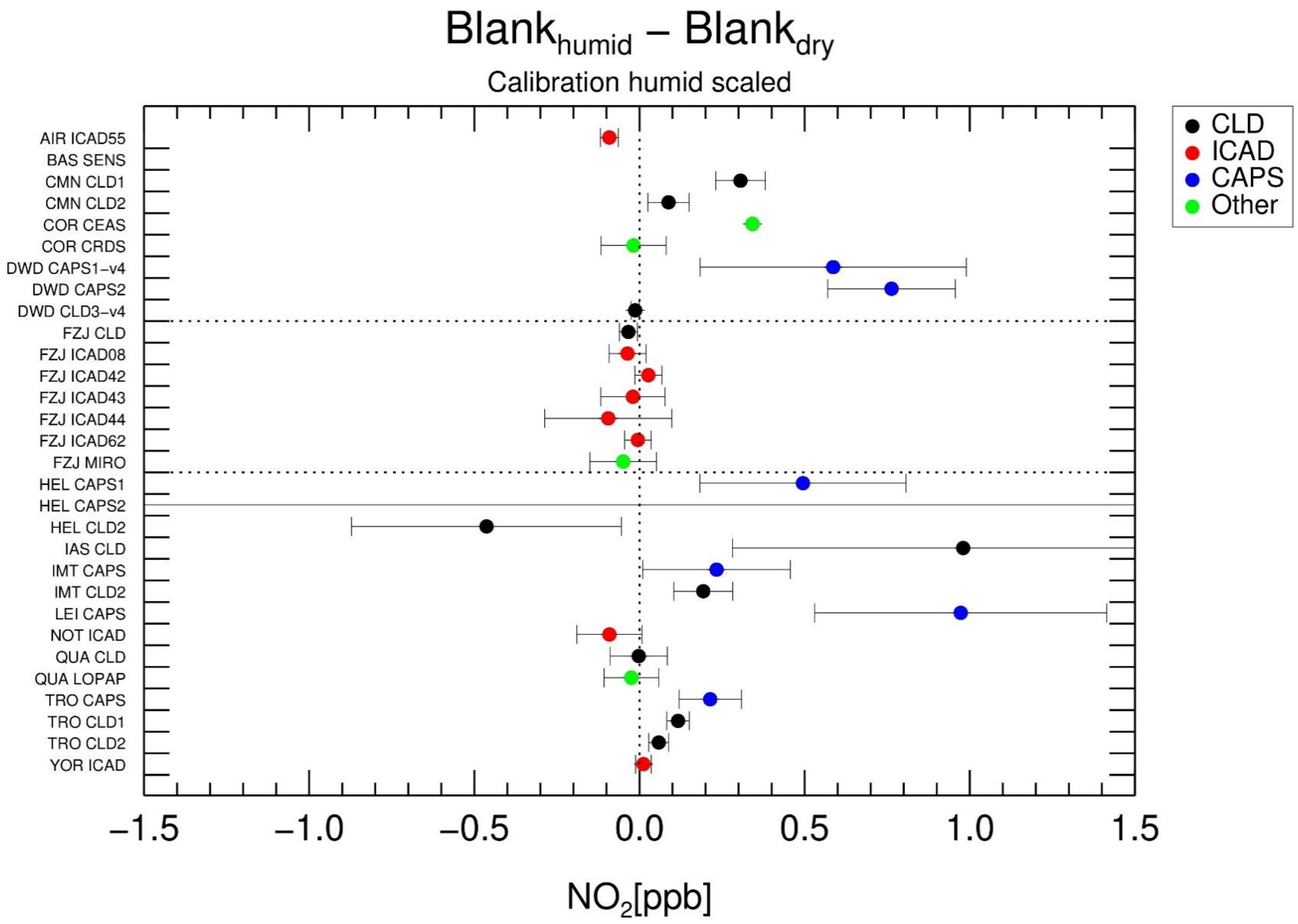
Measurements at zero



Effect of humidity on NO measurements



Effect of humidity on NO_2 measurements



Summary

- The experimental setup enabled to determine the instruments' sensitivities to within less than 1%
- Calibration is suggested for instruments with sensitivity outliers
- In general, the different measurement techniques measured close to the expected value
- Differences may exist among certain techniques, e.g. CAPS offset at 0

Outlook

- Further analysis of the experiments with ozone, HONO, glyoxal, formaldehyde, nitrites/nitrates, ambient air.

ACTRIS CiGas

Thank you!

ACTRIS
CiGas

Acknowledgements: This project received funding from the European Union's Horizon 2020 research and innovation agenda under grant agreement number 871115 and the German Bundesministerium für Bildung und Forschung.