Metrological performance assessment of different Cavity Enhanced Spectrometer to measure atmospheric nitrous oxide

O. Laurent[1], C. Philippon[1], C. Yver Kwok[1], L. Rivier[1], M. Ramonet[1]

[1] *Laboratoire des Sciences du Climat et de l'Environnement (LSCE)*

N2O Analyzers tested

ICOS compliant analyzer for N2O measurement :

Picarro G5310

LGR CO/N2O EP

ECOTECH Spectronus FTIR

Technology	Mid IR CRDS	Mid IR OA-ICOS	FTIR
Species	$N_2O/CO/H_2O$	$N_2O/CO/H_2O$	$N_2O/CO/CO_2/CH_4/\delta^{13}C\text{-}CO_2/\delta^{18}O\text{-}CO_2/H_2O$
Maintenance	coolant refill / 2 months	No maintenance	N_2 tank every 1 or 2 month, Mg perchlo
Dryer	Required	Required	Integrated (Nafion + $Mg(ClO_4)_2$)
Short Term Working standard (STWS)	At least 1 /day	At least 2/day	

Uncertainty Source

The N2O measurement **uncertainty** (bias and precision) **sources :**

- Temperature sensitivity
- Atmospheric pressure sensitivity
- H_2O measurement offset variability/drift
- Intrinsic variability (electronics, optics…)

→ Can be corrected with **a Short Term Working Standard (STWS)** measured regularly

- H_2O correction precision/bias
- H_2O correction drift
- H_2O sensitivity (slope) variability

→ **Dry** ambient air sample

- Linearity (calibration fit residuals)

→ Optimize the **calibration fit order**

- Spectroscopic cross sensitivity with other species

→ MLab assessment

- Uncertainty of assigned value of calibration scale

→ Optimize procedure (CAL FCL)

- Artifacts from Sampling system upstream analyzer

→ Regular assessment (shelter test…)

Improvement actions

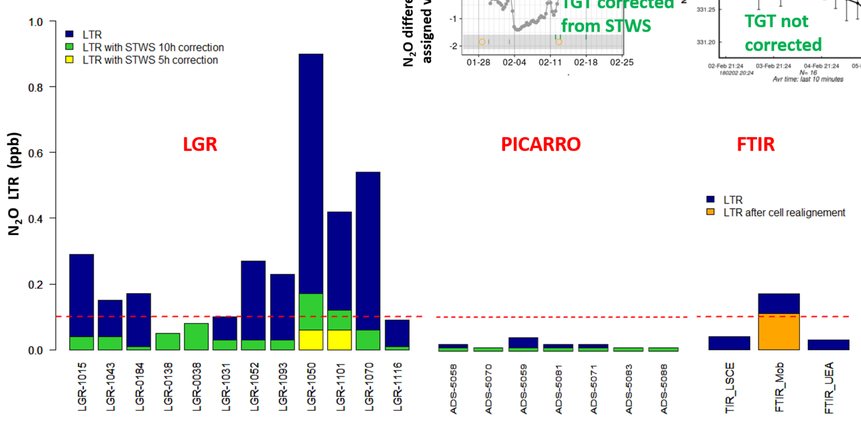
Once the improvement actions performed, the remaining uncertainties must be assessed

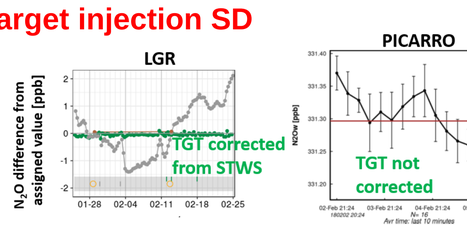
WMO Network compatibility goal : 0.1 ppb N_2O

Precision and Bias

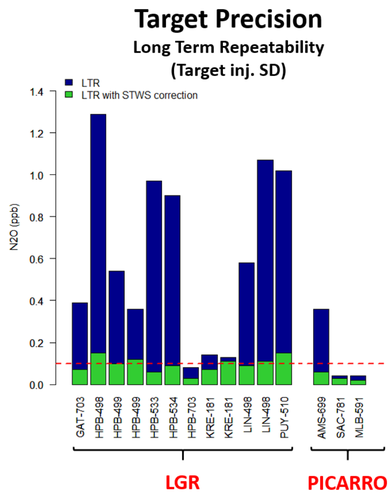
Long Term Repeatability (**LTR**) = **Target injection SD**

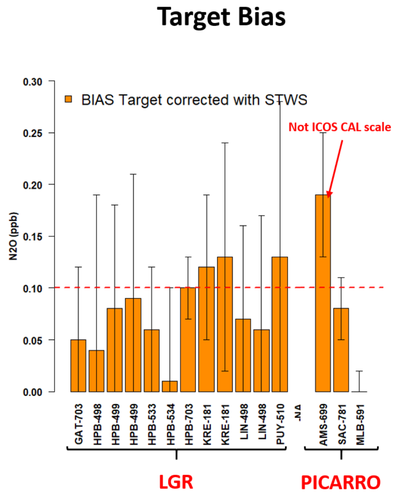
- **At ICOS Metrological Lab**





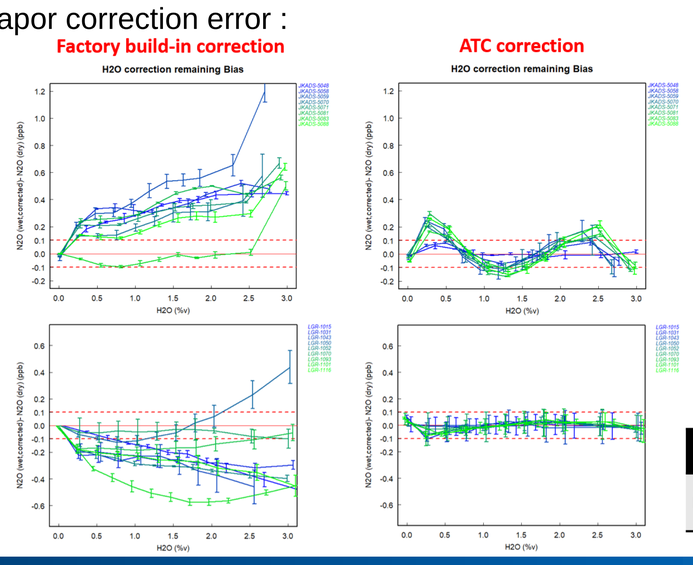
- **In the Field (several months)**

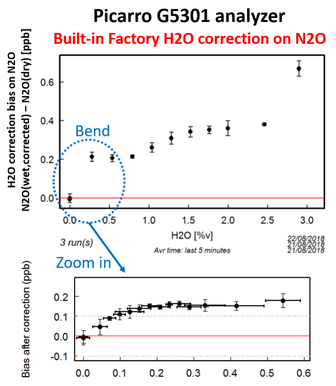




Water vapor

Water vapor correction error :





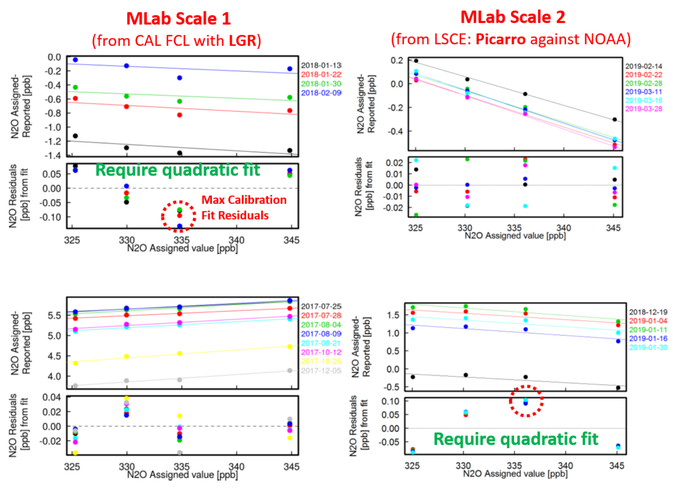
Any H2O variability (e.g. temperature variability arround Nafion dryer) in the bend area induce a N2O error variability.

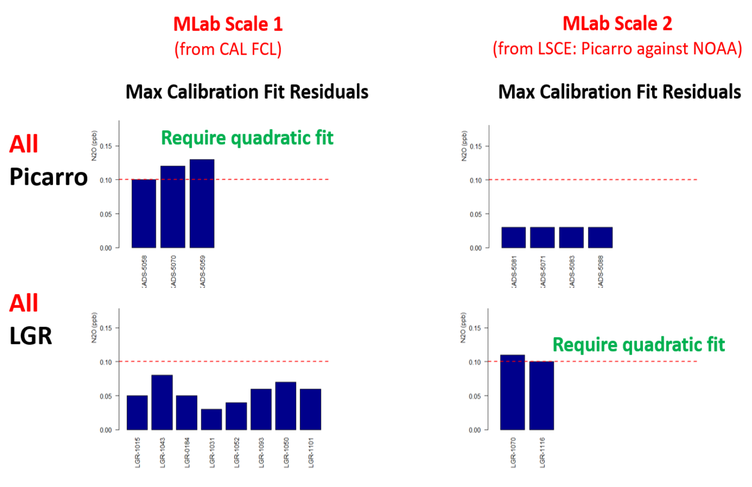
Note: Drying technique such as Nafion induce a small bias (up to -0,3 ppb depending for Nafion PD model). However passing Calibration gas through Dryer should correct most of the bias.

		NO dryer Factory	NO dryer ATC	Cryo	Nafion Only for amb. air	Nafion For Cal. & amb. air
Max H2O corr error on N2O (ppb)	Picarro	0.6	0.3	0	0.2	0.05
	LGR	0.6	0.15	0	0.15	0.05

Linearity

Applied Calibration fit order: **1**



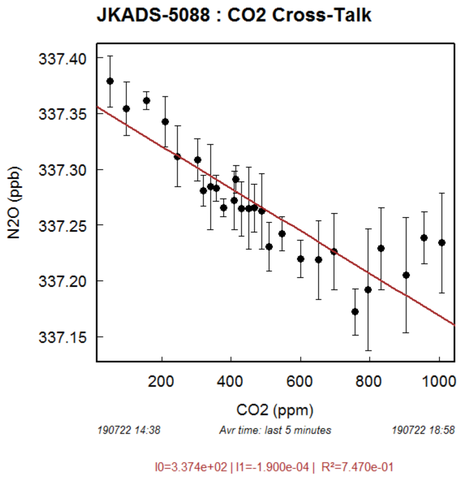


	Picarro	LGR	FTIR
Linearity error (ppb) Typical/Max	0.03/0.1	0.03/0.1	0.05/0.15

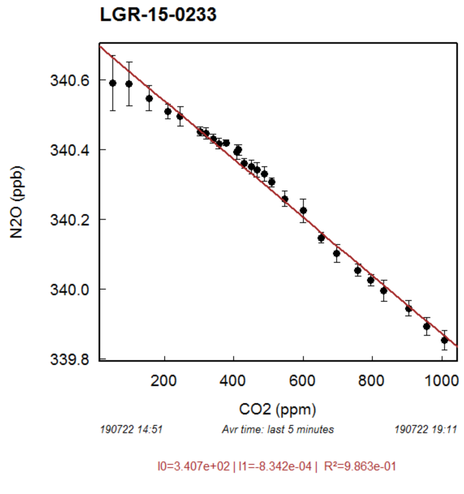
Picarro and LGR show a different Linearity (cross sensitivity with another air species?). An unappropriated calibration fit order can induce a significant error.

CO_2 cross sensitivity

Picarro



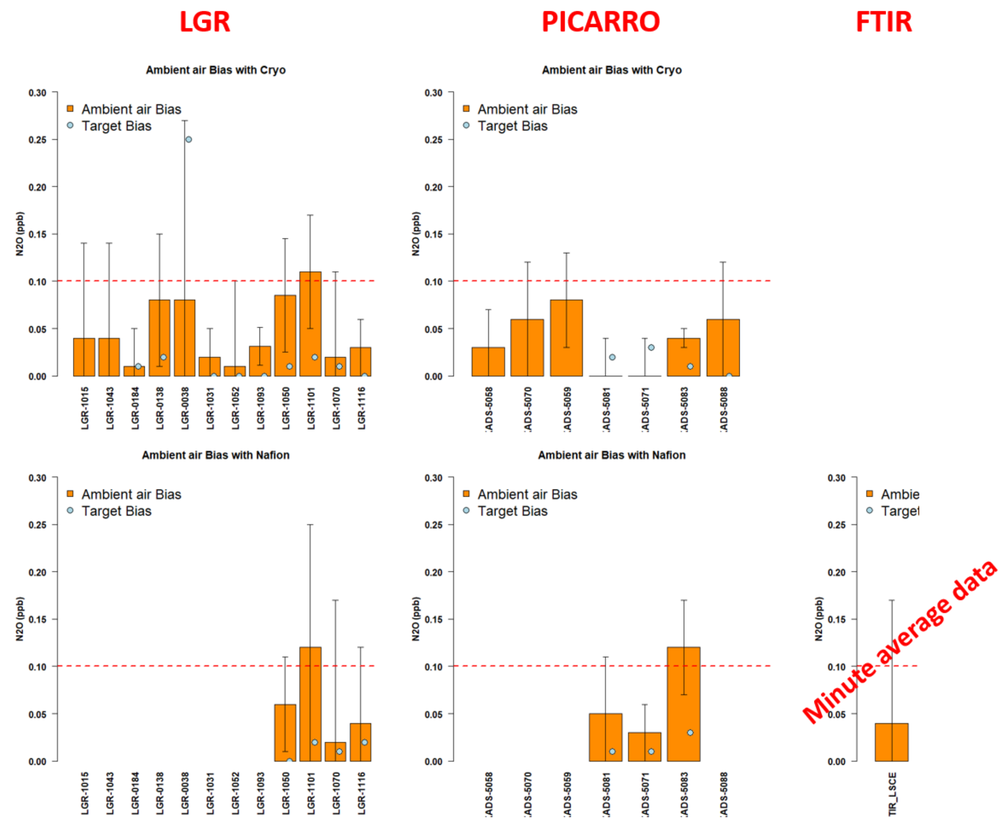
LGR



Validation in ambient air

Hourly average data
STWS corrected.

N2O Reference:
Picarro with cryo and 5h STWS



Uncertainty Budget

	Picarro	LGR	FTIR
H2O correction error with Nafion (ppb) Typical/Max	0.02/0.05	0.02/0.05	0
Remaining Nafion artifacts (ppb) Typical/Max	0.01/0.03	0.01/0.03	0.01/0.03
Linearity error (ppb) Typical/Max	0.03/0.1	0.03/0.1	0.05/0.15
Precision with STWS correction (ppb) Typical/Max	0.02/0.07	0.07/0.15	0.05/0.15
Overall Uncertainty (ppb) Typical/Max (Quadrature sum)	**0.04/0.13**	**0.08/0.19**	**0.07/0.21**