Evaluation of the PICARRO G1301 (previously called EnviroSense 3000i) for CO2/CH4 continuous measurement

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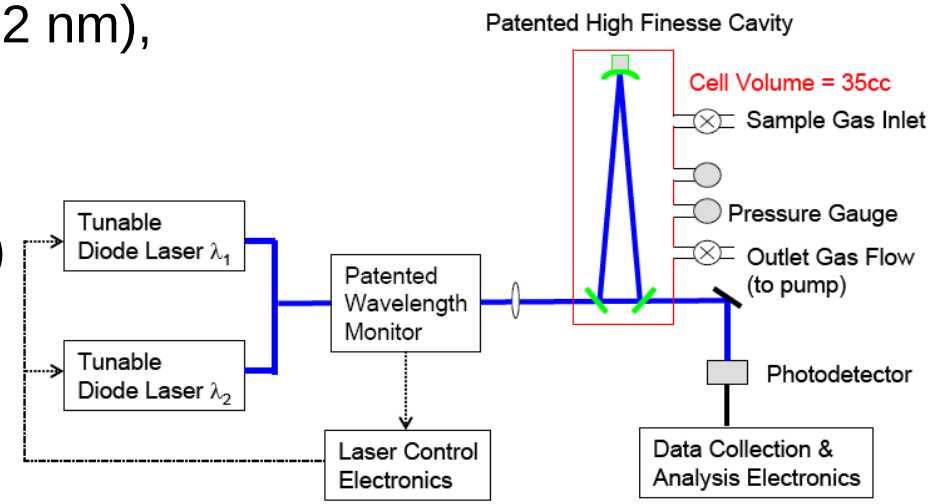
Overview of the instrument

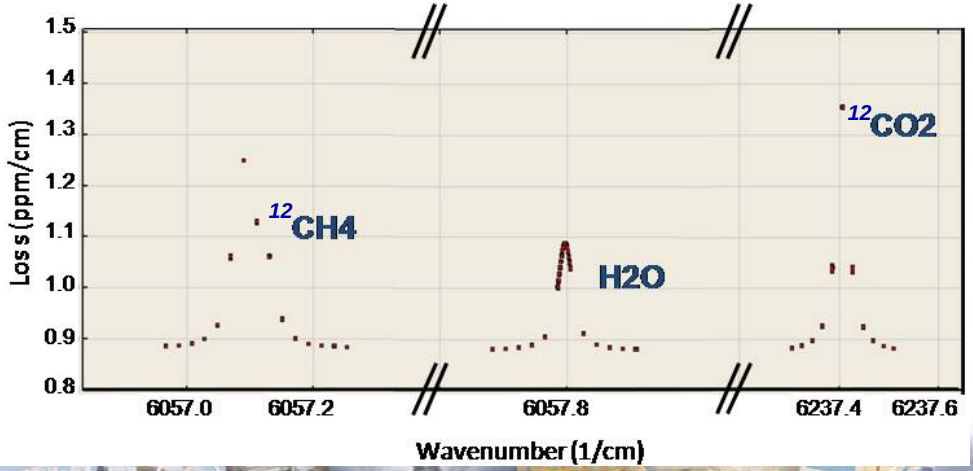
- Designed to measure continuously (0.2 Hz) CO2, CH4 and H2O
- Consists of 3 modules : 1 PC, 1 Data Acquisition System and 1 Pump Vacuum Unit
- Implemented with a multiposition Valco valve for gas distribution

Overview of the instrument

- 2 DFB diodes used, one for $^{12}CO2$ (1602 nm), one for $^{12}CH4$ and H2O (1651 nm)
- Precise control of the wavelength injected inside the cavity (± 0.0001 cm^{-1})
- V-shape optical cavity composed of 3 mirrors

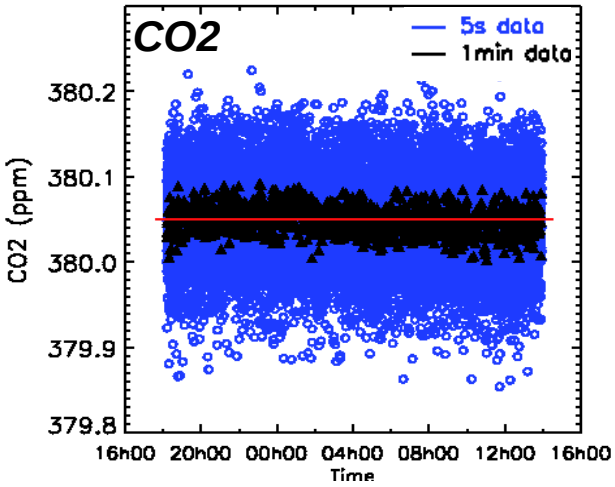


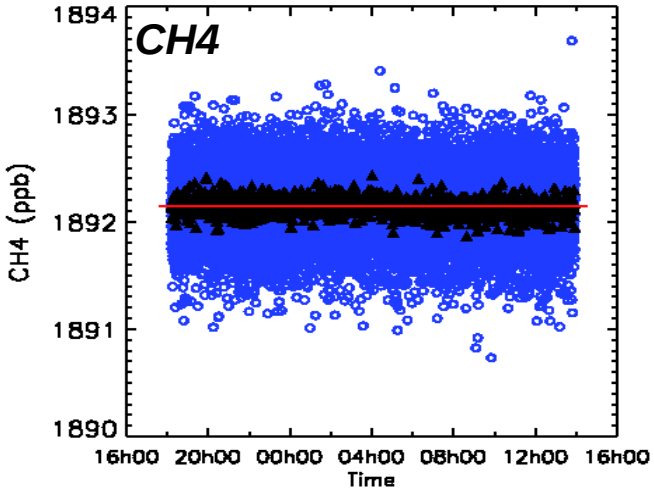
- "Wavelength-Scanned" CRDS: ring down times are measured as function of wavelength → gas sample optical spectra generated → absorber concentrations deduced



Precision Assesment

- Estimated from the measurement of a calibration gas for about 19 hours :





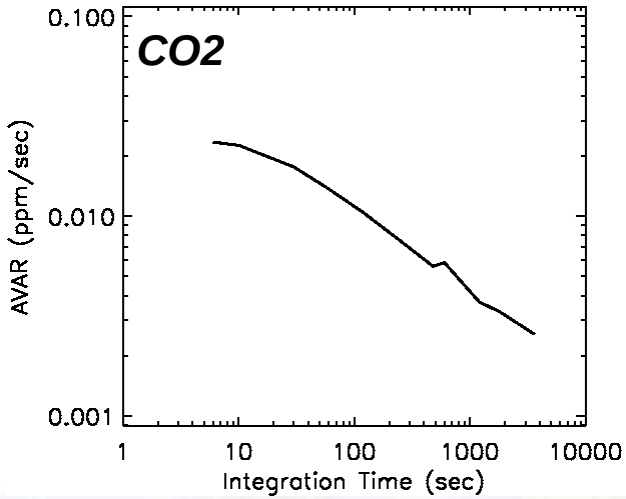
CO2 (ppm)

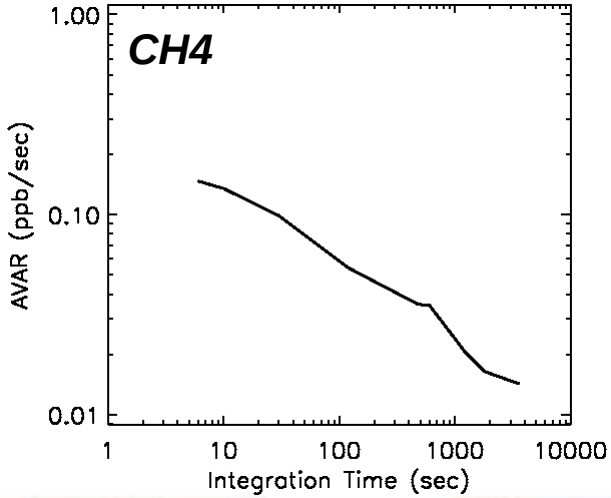
5s data: **380.05 ± 0.048**
1min data: **380.05 ± 0.016**

CH4 (ppb)

5s data: **1892.15 ± 0.30**
1min data: **1892.15 ± 0.08**

- Allan Variance:

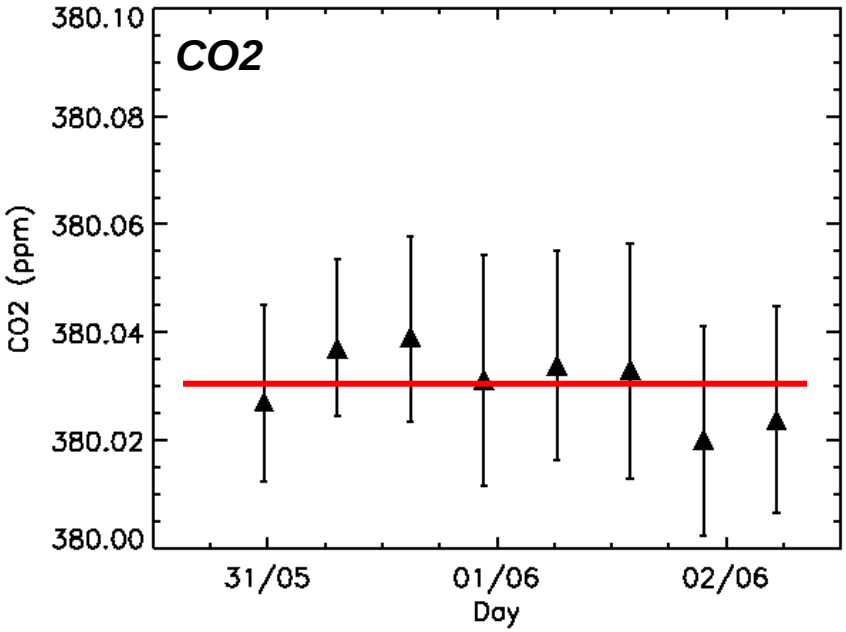


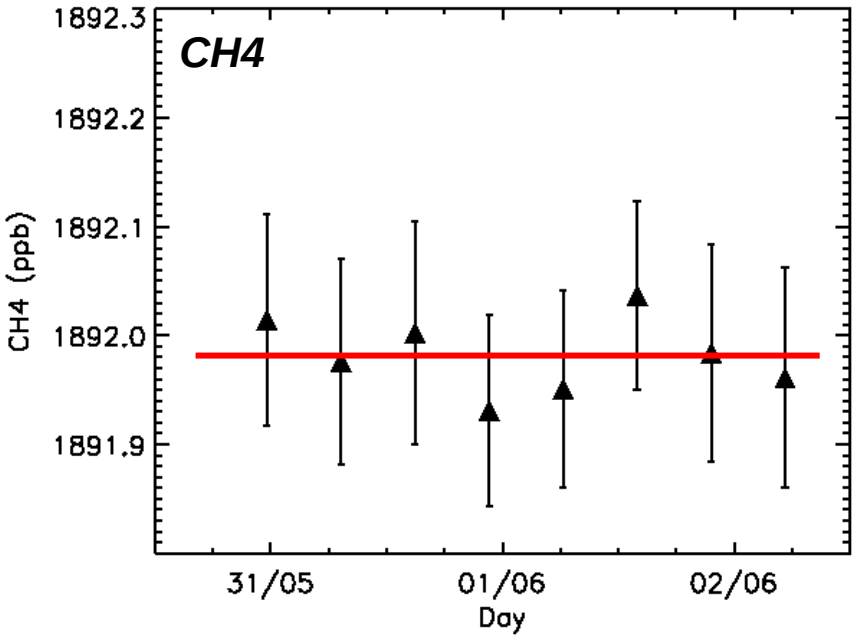


→ No instrumental drift effect observed

Repeatability Assesment

- Estimated from the repeated measurement of a calibration gas for 40 minutes every 7 hours over a 2 day period:



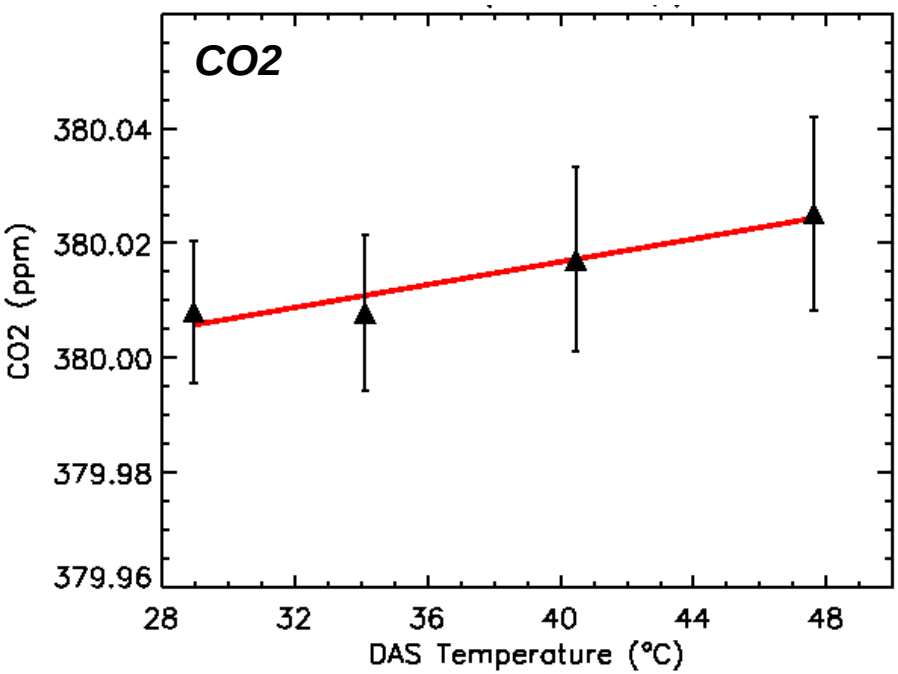


<CO2> = 380.03 +/- 0.01 ppm

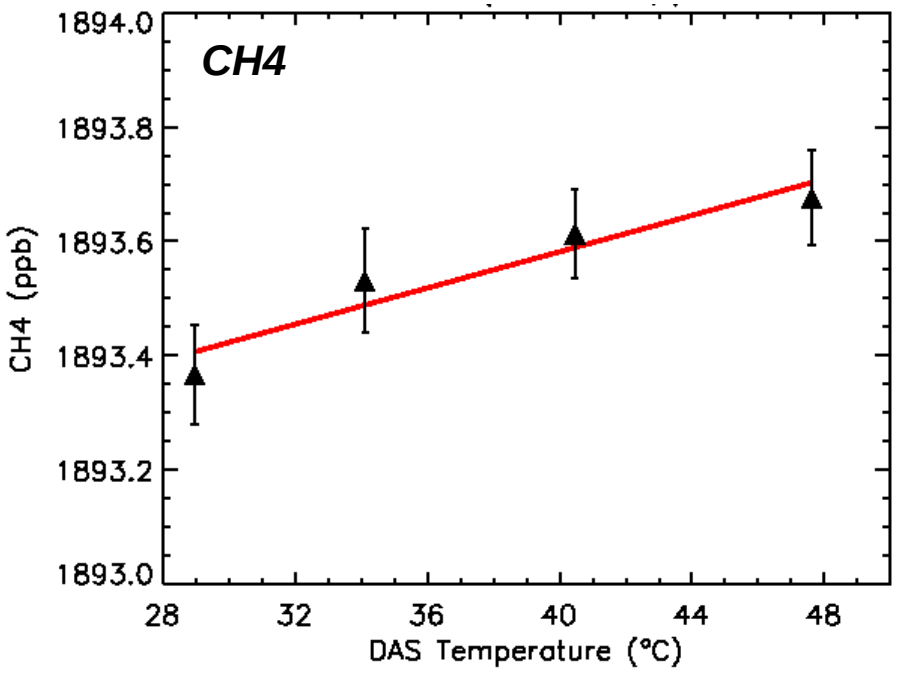
<CH4> = 1891.98 +/- 0.04 ppb

Sensitivity to temperature

- Experience: Analyser put into a rack. Temperature inside the rack controlled via 2 heater plates. Calibration gas measured for 4 different “ambient” temperatures (each time for 1 hour)



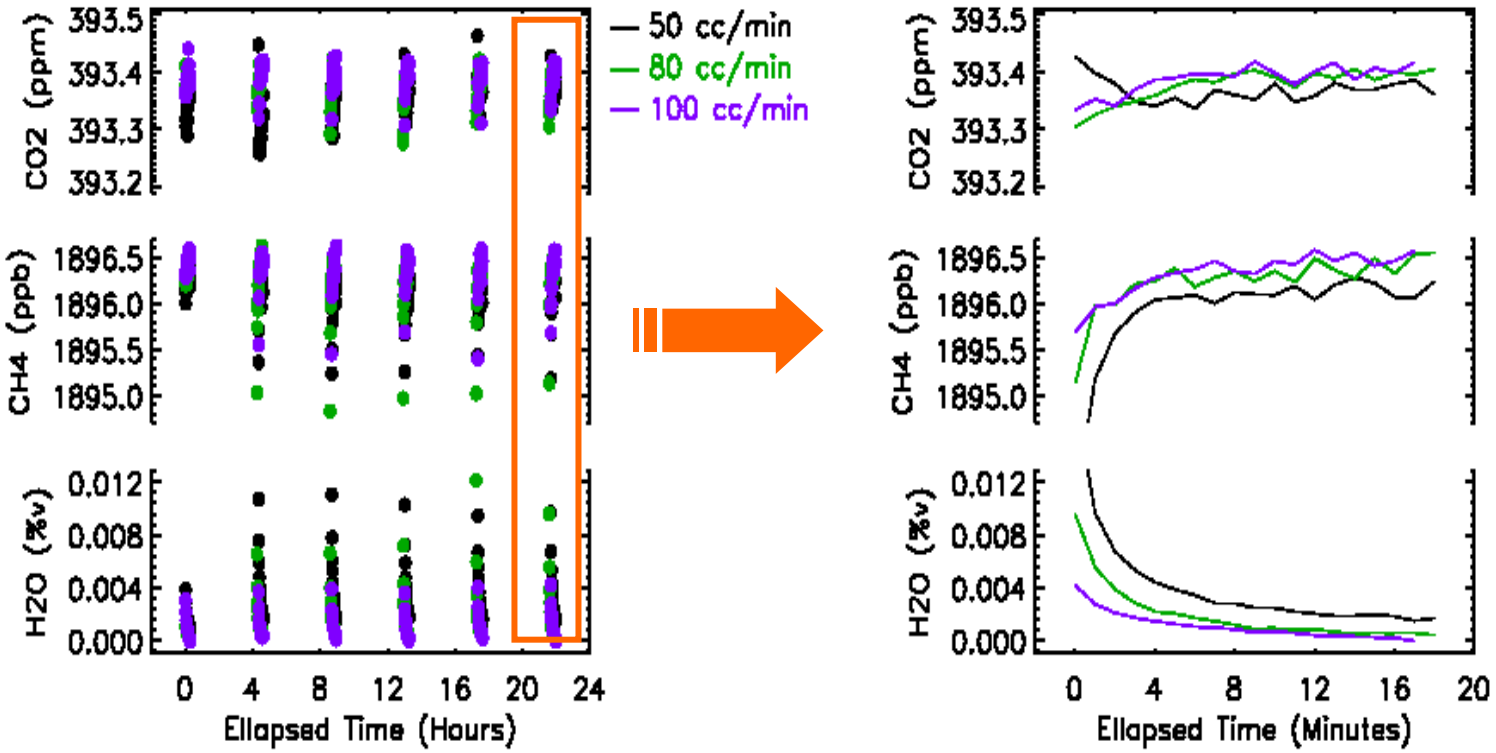
+ 0.001 ppm / °C



+ 0.02 ppb / °C

Sensitivity to flow rate

- Experience: one calibration gas measured alternately with “wet” ambient air for 20 minutes every 4 hours ; 3 flow rates tested (50, 80 & 100 cc/min)



Sensitivity to water vapour

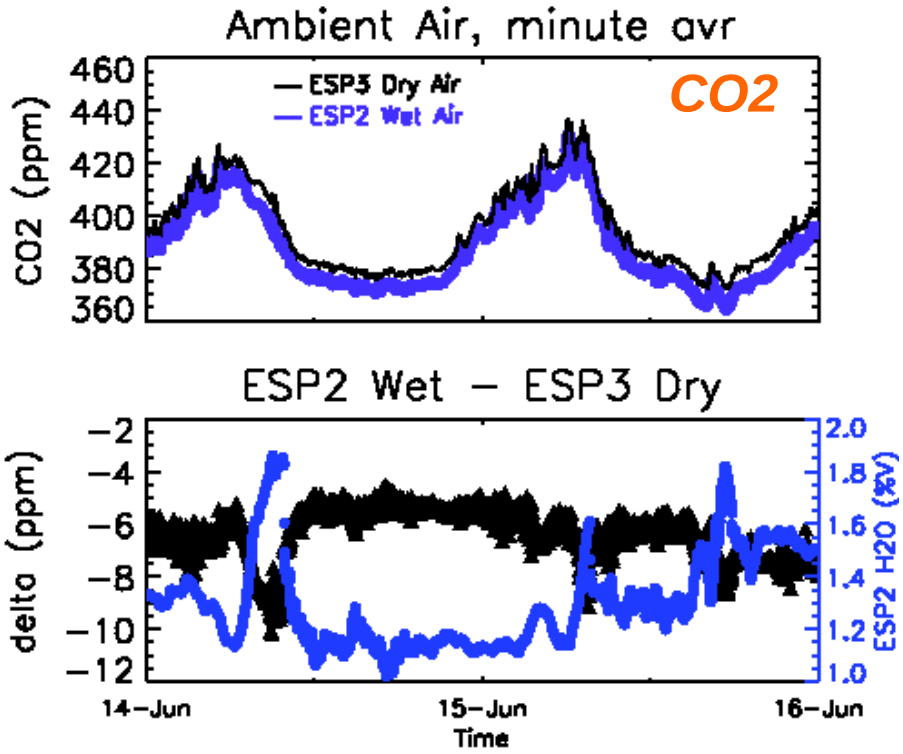
- Water vapour interferes due to dilution and spectral line broadening effects.
- PICARRO established a correction for CO2 based on a comparison between dry and wet ambient air measurements :

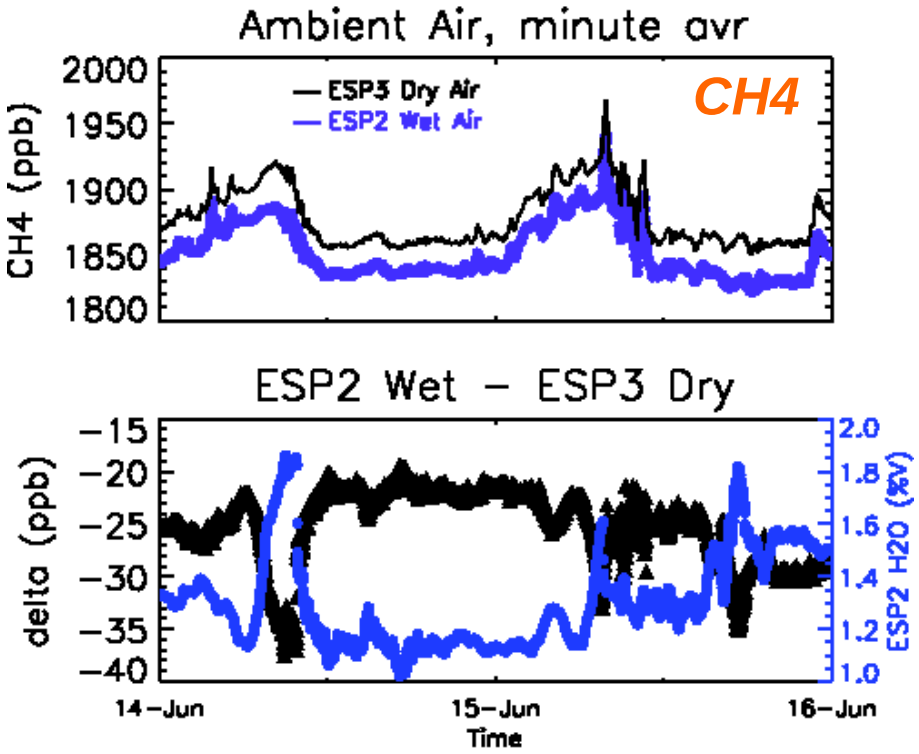
$$(CO_2)_{cor} = \frac{(CO_2)_{raw}}{1 - 0.01244 \times H_2O}$$

- But no correction for CH4 …
- Objectives:
  - Check for the validity of the water correction
  - Try to find a way to correct CH4

Sensitivity to water vapour

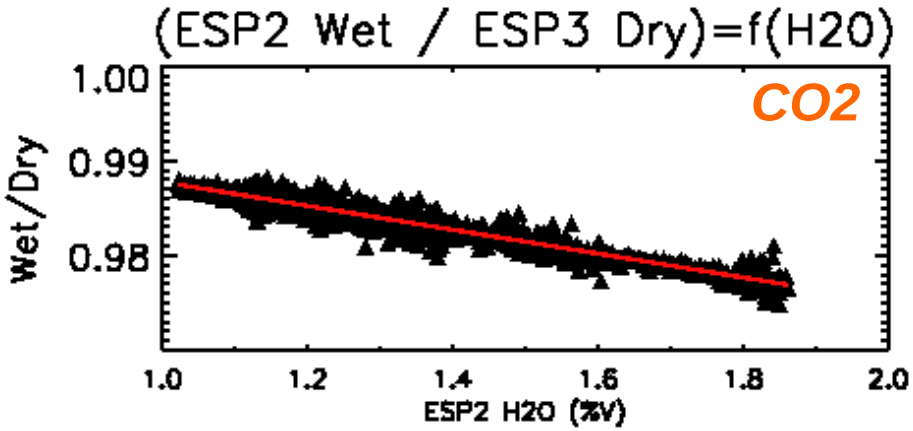
- Experience: 2 EnviroSense instruments measuring the same ambient air, but for one air was dried (cryocooler)

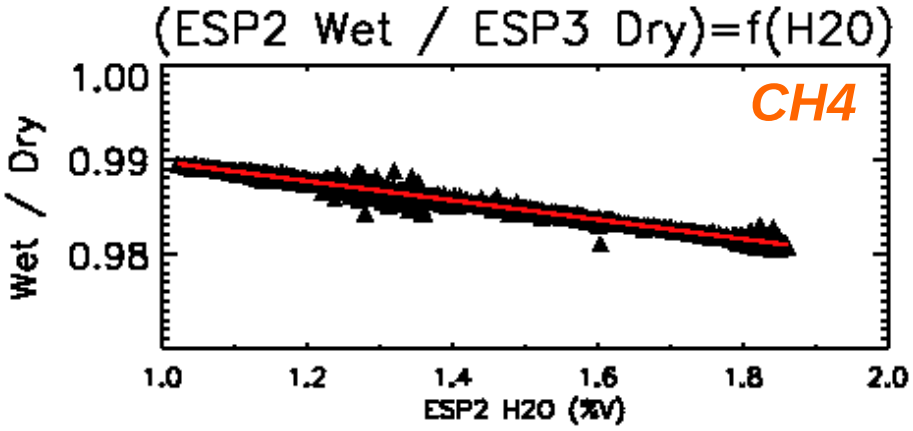




Sensitivity to water vapour

- We plotted Wet/Dry measurements = f(H2O):





$$(CO_2)_{cor} = \frac{(CO2)_{raw}}{1 - 0.0126065 \times H_2O}$$

$$(CH_4)_{cor} = \frac{(CH_4)_{raw}}{1 - 0.0102018 \times H_2O}$$

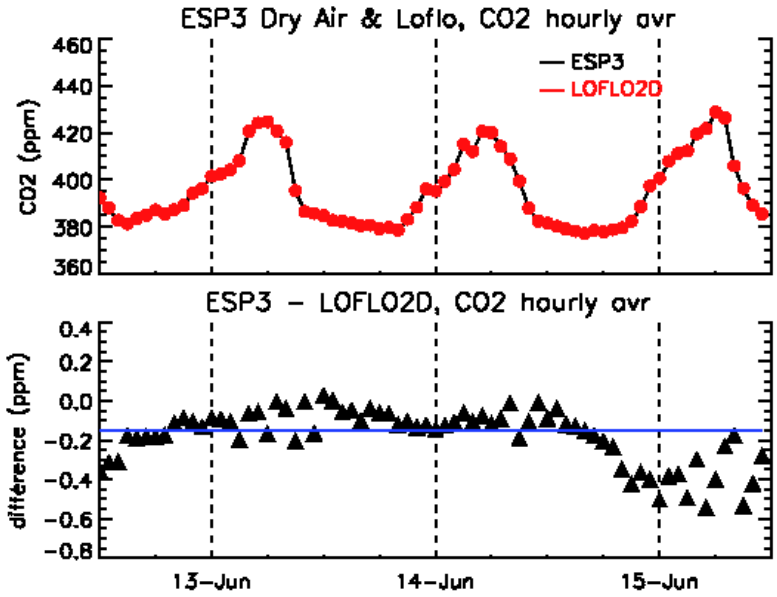
→ "LSCE" correction for CO2 very closed to the one from PICARRO

CH4 can be water corrected like CO2

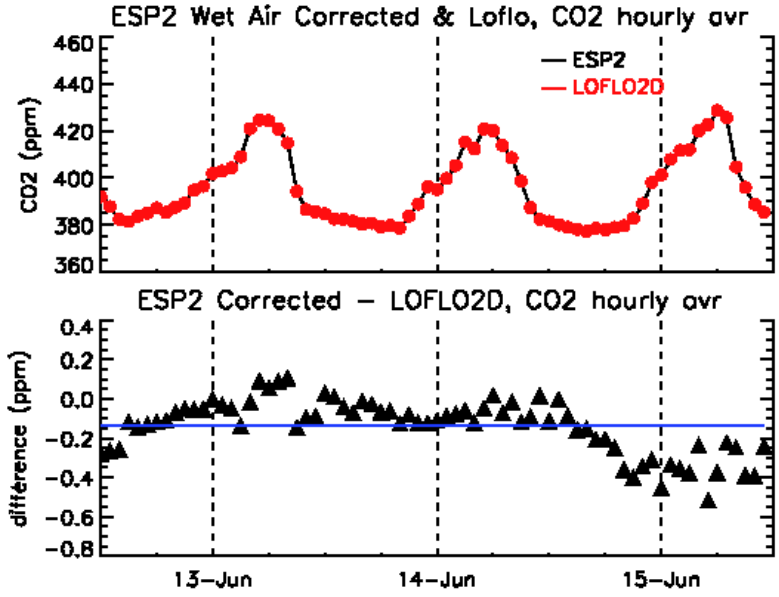
Validity of these equations ??

Comparison with the LOFLO2D

- Ambient air comparison between our LOFLO2D instrument, one EnviroSense measuring dry ambient air and one EnviroSense measuring wet ambient air:



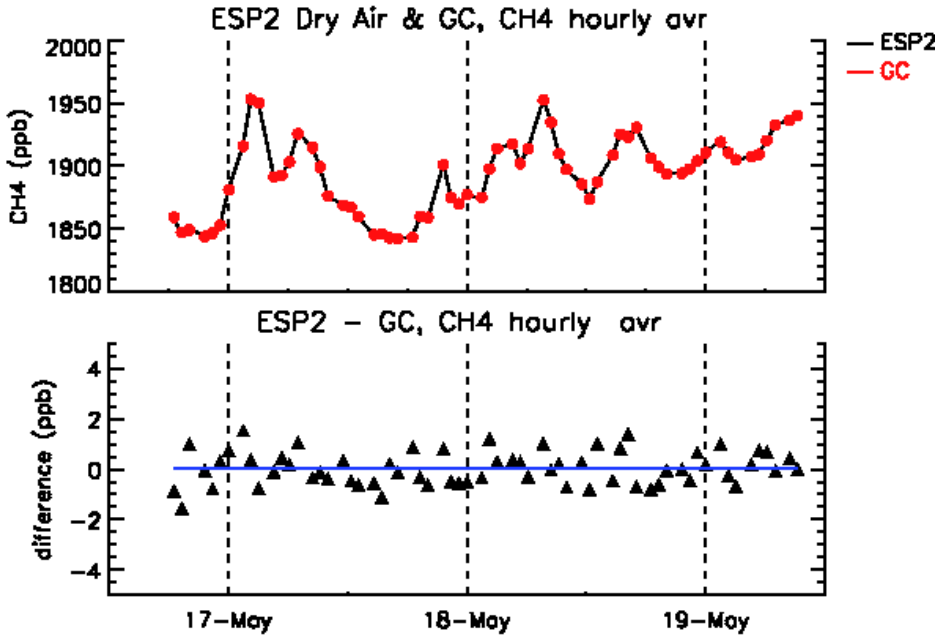
With “dry” EnviroSense:
Mean diff. = -0.15 ±0.14 ppm

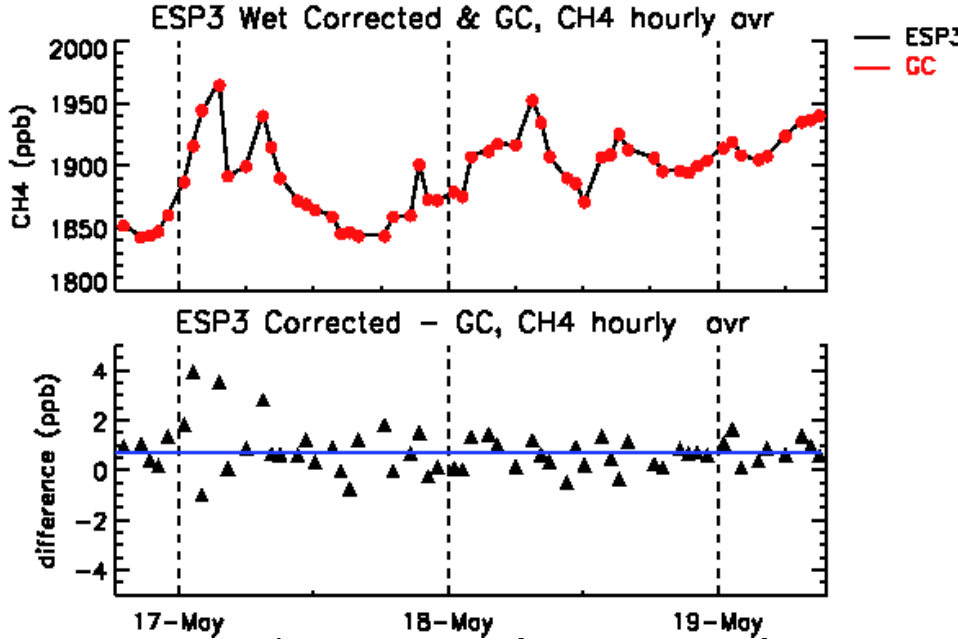


With “wet” EnviroSense:
Mean diff. = -0.14 ±0.14 ppm *(PICARRO correction)*
Mean diff. = -0.20 ±0.14 ppm *(LSCE correction)*

Comparison with the GC

- Ambient air comparison between our GC instrument, one EnviroSense measuring dry ambient air and one EnviroSense measuring wet ambient air:





With “dry” EnviroSense:
Mean diff. = 0.04 ±0.67 ppb

With “wet” EnviroSense:
Mean diff. = -11.1 ±1.8 ppb *(without correction)*
Mean diff. = 0.8 ±0.9 ppb *(LSCE correction)*

Calibration

- Factory calibration by Picarro :

  → H2O: bubbler to create 100% relative humidity samples that are then diluted with a mass flow controller to different humidity levels

  → CO2 and CH4: low cost artificial mixture cylinders of CO2 and CH4 in air are used (δ13CO2 ≈ -40 pm et δ13CH4 ≈ -40 pm).
  NB : instrument measures 12CO2 and 12CH4 spectral line but it is calibrated to report the total concentration of the CO2 and CH4.

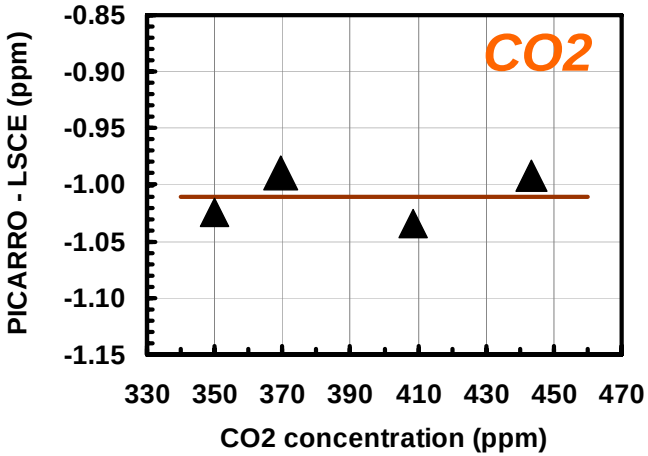
- Calibration at LSCE:

  4 tanks filled with dry natural air, prepared in Jena, calibrated by our LOFLO2D against WMO x02 scale for CO2 and by our GC system against WMO x02 scale for CH4.

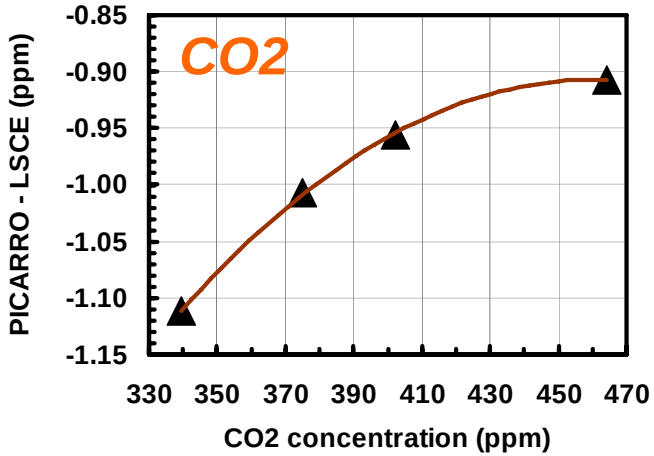
- Calibration at Lamto:

  4 tanks filled with synthetic air, prepared by Steininger, calibrated by our LOFLO2D against WMO x02 scale for CO2 and by our GC system against WMO x02 scale for CH4.

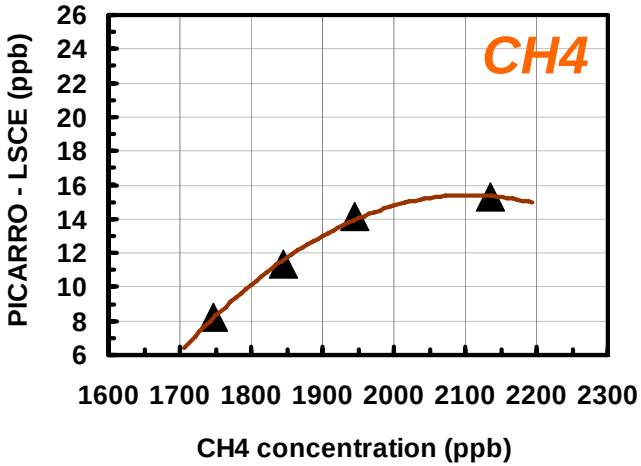
Calibration

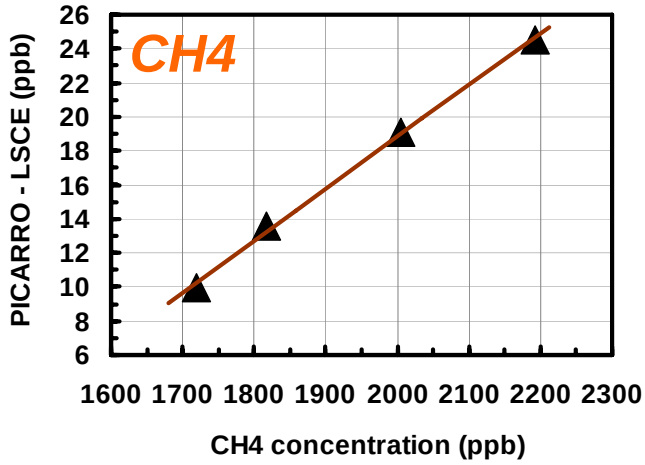


At LSCE, with 4 cylinders filled with “natural” air



At Lamto, with 4 cylinders filled with synthetic air





Conclusion

- High level performance instrument:
  precision: 0.02 ppm for CO2 / 0.1 ppb for CH4
  repeatability: 0.01 ppm for CO2 / 0.05 ppb for CH4
  no significant drift observed over a 2 month period
- No major influence of the ambient temperature
- Flow rate dependence to be considered when using a multi-position valve
  → influence on time stabilisation (a 100 ml/min recommendation)
- Remaining issues:
  - Water correction for CH4
  - Validity of the water correction equations
  - Sensitivity to 13C isotopic ratios and to gas composition