GOBIERNO DE ESPAÑA
MINISTERIO DE AGRICULTURA Y PESCA, ALIMENTACIÓN Y MEDIO AMBIENTE
AEMet Agencia Estatal de Meteorología

CO_2, CH_4, and CO with CRDS technique at the Izaña Global GAW station: instrumental tests, developments and first measurement results

Angel J. Gómez-Peláez, Ramón Ramos,
Vanessa Gómez-Trueba, Emilio Cuevas,
Enrique Reyes

Izaña Atmospheric Research Center,
Meteorological State Agency of Spain (AEMET)

GGMT-2017, 27-31 August 2017, Dübendorf, Switzerland

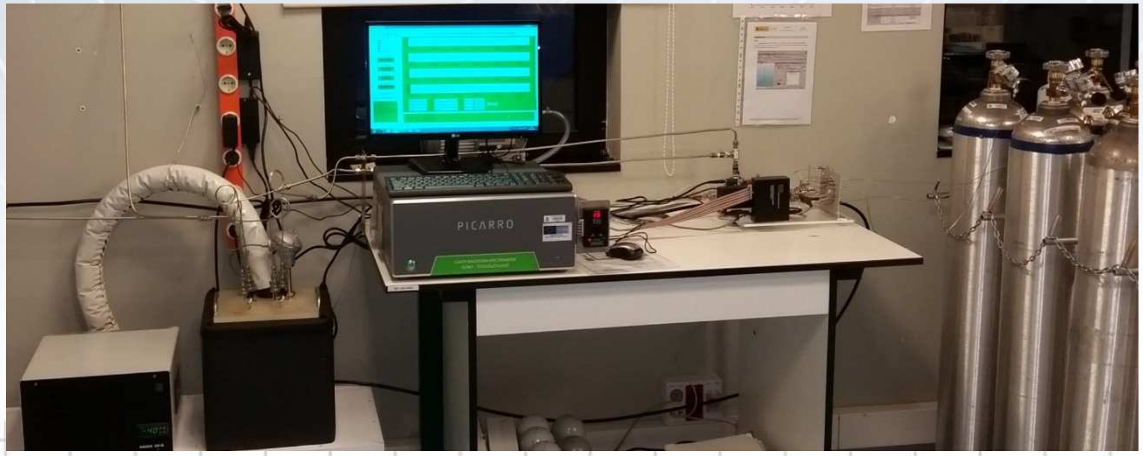
Acquisition of a CRDS for CO_2, CH_4 and CO

GOBIERNO DE ESPAÑA
MINISTERIO DE AGRICULTURA Y PESCA, ALIMENTACIÓN Y MEDIO AMBIENTE
AEMet Agencia Estatal de Meteorología

- At the end of 2015, a **CO2/CH4/CO CRDS** was installed at the Izaña Global GAW station (Tenerife, Spain) to improve the Izaña GHG GAW measurement programme.
- The acquisition of the instrument was largely financed by European FEDER funds through a Spanish R+D infrastructure project we got: “Equipamiento para la Monitorización e Investigación en la estación Global VAG (Vigilancia Atmosférica Global) de Izaña (Tenerife) de componentes atmosféricos que provocan y modulan el cambio climático” AEDM15-BE-3319.

European Union

European Regional Development Fund
“A way to build Europe”



Initial/Acceptance tests performed to the CRDS
November 2015

- **Precision test** (ICOS): measuring a gas cylinder (filled with dry natural air) over **25 hours**; first hour rejected (stabilization time). **Good results**:

	Raw data average length	CO2	CH4	CO
Std. Dev. (1-sigma)	1 minute	0.013 ppm	0.19 ppb	0.87 ppb
	60 minutes	0.009 ppm	0.14 ppb	0.16 ppb

- **Repeatability test** (ICOS): Measuring alternately a gas cylinder (filled with dry natural air) during 30 minutes and ambient air (not dried) during 270 minutes over **72 hours**. Statistics based on the last 10 minute average data of each cylinder injection.

We use 2 cylinders (each one measured every 5 hours). **Good results**:

	CO2	CH4	CO
Std. Dev. (1-sigma) 10' average raw data	0.016 ppm	0.23 ppb	0.23 ppb
	0.016 ppm	0.23 ppb	0.35 ppb

- **Ambient pressure sensitivity of the measurements during the 72-h test**: **CO**: 0.4 ppb/10mb; **CO2**: 0.038 ppm/10mb; **CH4**: 0.47 ppb/10mb

Initial/Acceptance tests performed to the CRDS
November 2015

- **Inlet pressure sensitivity** when measuring a gas cylinder filled with dry natural air:

CO: 0.1 ppb/6 psi; CO2: 0.04 ppm/6 psi; CH4: 0.16 ppb/6 psi

The sensitivity for CO2 is quite large.

- **Fitting response curves when calibrating with 4 WMO tertiary standards**:

Linear fitting for CH4. **RMS residual = 0.143 ppb**. Excellent.

Linear fitting for CO. **RMS residual = 0.067 ppb**. Excellent.

Linear fitting for CO2. RMS residual = 0.0395 ppb. Worse than our NDIR-based system with cuadratic fitting.

Quadratic fitting for CO2. RMS residual = 0.0284 ppm. Still slightly worse than our NDIR-based system.

Quadratic fitting for CO2 correcting aproximately from outletvalve aperture (related with the inlet pressure). **RMS residual = 0.0219 ppm**. Good. There were small differences in the inlet pressure for air of the different cylinders (we have improved our skills getting smaller differences between them since then).

Calibrations and Response Functions

- **Calibration scheme**: 4 standards + 2 target gases. 30 minutes per tank every cycle.

- From Dec. 2015 till Aug. 2016: **5 cycles** per calib. A calib. **every 3 weeks**.

- From Sept. 2016 till present : **2 cycles** per calib. A calib. **every month**. Enough.

The regulators of the standards remain closed between calibrations.

For CO_2 and CH_4, the **last 10 mins** of each injections are used. For CO, the **last 20 mins**. Stabilization times more than enough (numeric details not presented here).

I have developed a Fortran 90 code for processing the calibrations. We **use raw values** (not dry values).

- **Long-term drift of the CRDS**. Raw response drifts for a **virtual tank** with 400 ppm of CO_2, 1850 ppb of CH_4 and 100 ppb of CO:

CO_2	CH_4	CO
0.104 ppm/year	2.22 ppb/year	0.544 ppb/year

- Using the empirical sensitivities (partial derivatives) provided in Sect. 3.3.6 of Yver Kwok et al. (2015), we have determined that **our CRDS has a long-term drift of 0.152ºC/Torr and 0.446 Torr/year in the cavity sensors**.

Calibrations and Response Functions

GOBIERNO DE ESPAÑA — MINISTERIO DE AGRICULTURA Y PESCA, ALIMENTACIÓN Y MEDIO AMBIENTE — AEMet Agencia Estatal de Meteorología

- **Raw signal used**: **raw CO2** (**not dry**), **raw CH4** (**not dry**), and since the raw CO value is not provided by the CRDS (but only the dry one), we compute, using peak84_raw, peak_14 and b_h2o_pct, **an uncalibrated raw CO value not dry** (indeed, **peak84_spec_wet**) corrected only from CO2 and H2O baseline interference (Rella, 2016, Private communication).

- **Response functions used**:

For CH4 and CO, a linear function:

C_raw = a + b * C, where C is the real dry mole fraction (the gas standards are dry), and C_raw the raw signal.

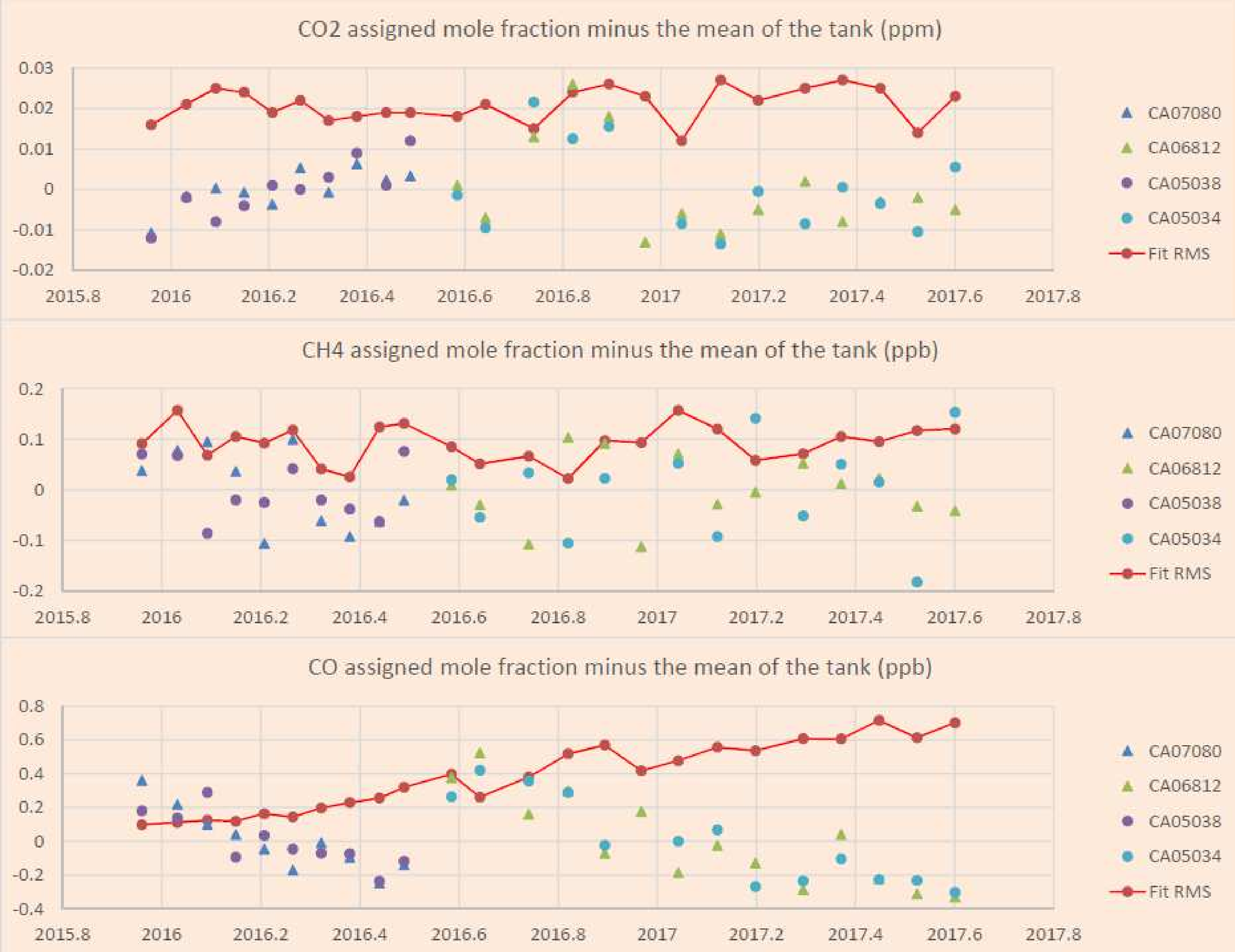
For CO2, a quadratic function with raw signal slightly corrected in outletvalve aperture (OV):

CO2_raw + (OV-26468.15)*0.04/7700= a + b * CO2 + c * CO2^2

Calibration and Response Functions

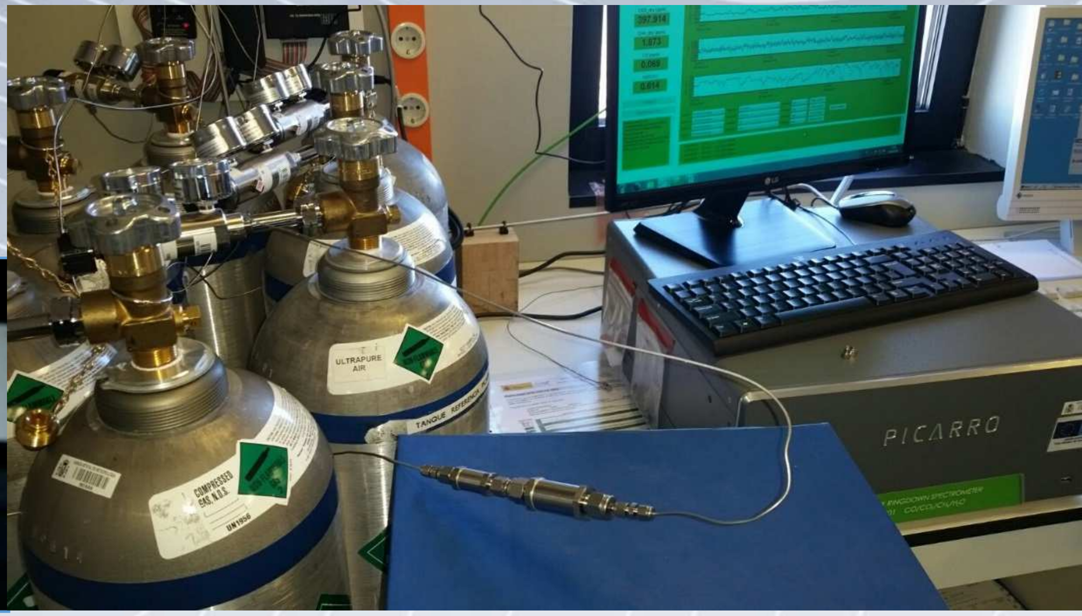
GOBIERNO DE ESPAÑA MINISTERIO DE AGRICULTURA Y PESCA, ALIMENTACIÓN Y MEDIO AMBIENTE

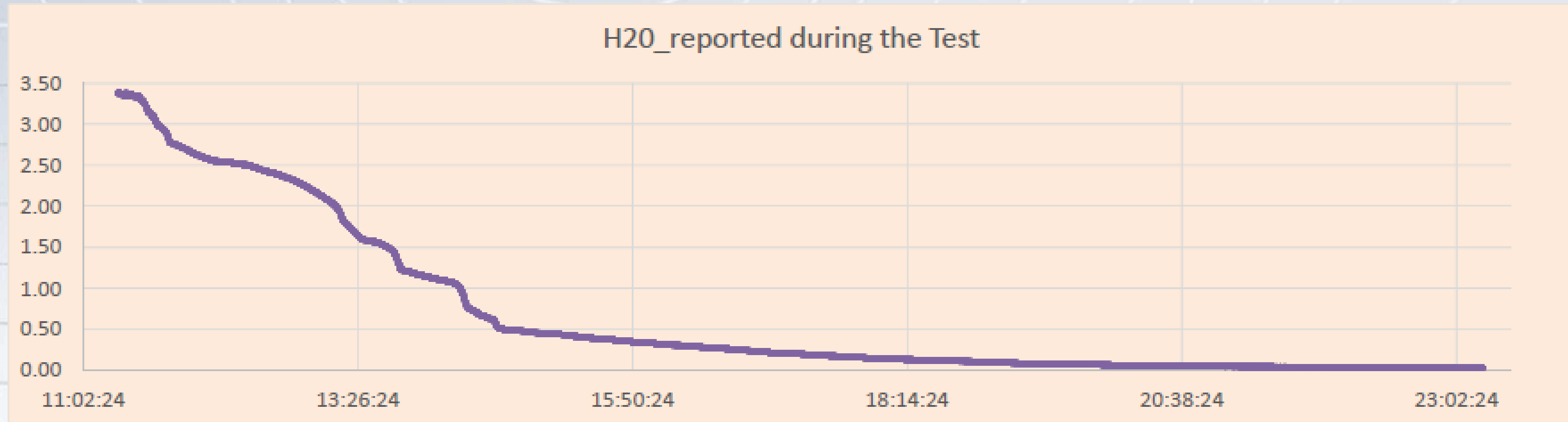
AEMet Agencia Estatal de Meteorología



Water Vapour Correction: water droplet method

Crushed (to increase the Surface/volumen ratio) **Silica Gel balls soaked with deionized water**

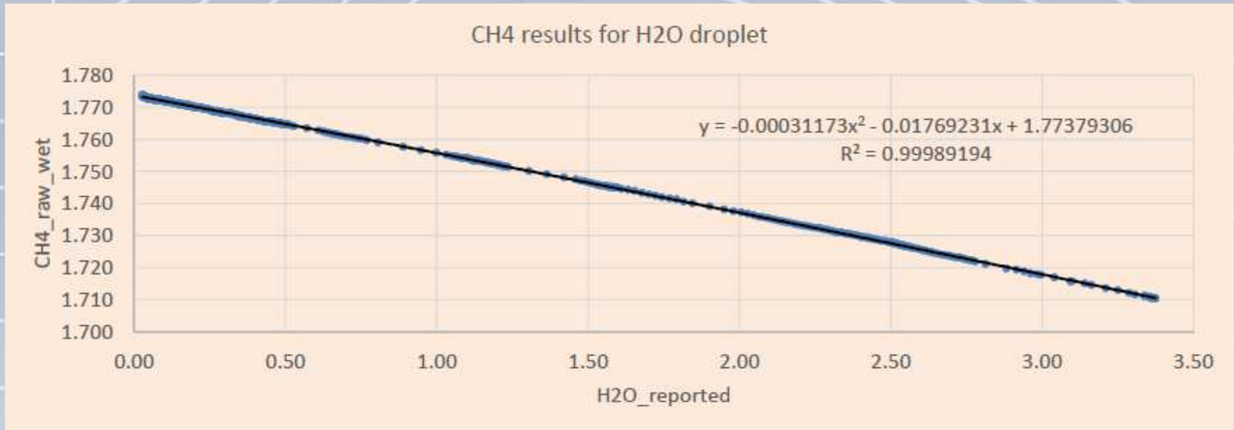




Water Vapour Correction: water droplet method

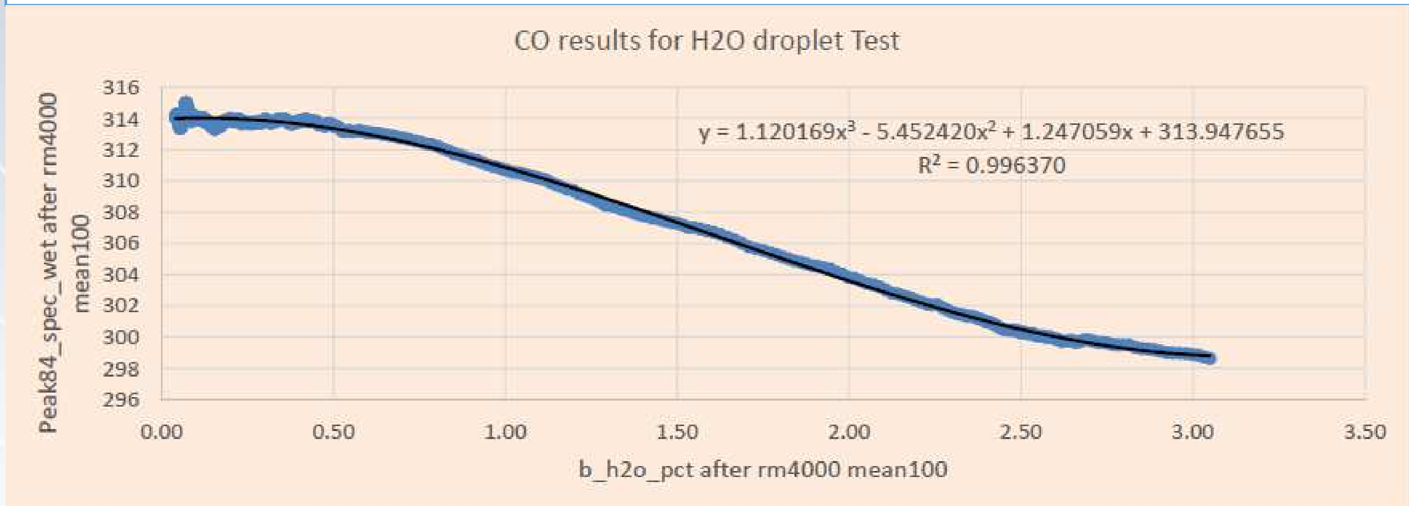
Our correction function is similar to that of Chen et al. (2010). Indeed, for **CO2** we use exactly their function.

GOBIERNO DE ESPAÑA
MINISTERIO DE AGRICULTURA Y PESCA, ALIMENTACIÓN Y MEDIO AMBIENTE
AEMet Agencia Estatal de Meteorología



We use means of 100 instantaneous values for all the variables

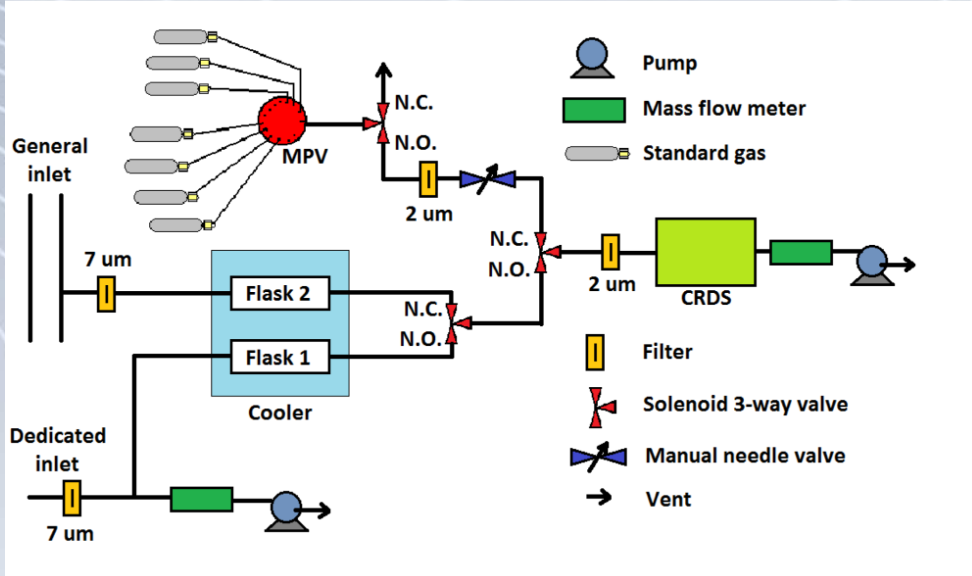
CO signal is very noisy, but the long duration of the experiment allows us using **4000-instantaneous-value running means** without compromising the accuracy of the data:



We use a cubic correction function for CO

Ambient Measurements

- Ambient air/gas standard **plumbing configuration** operative since 28 Nov 2016.
- Before that date, there were no “Dedicated inlet”, **no drying** (no cooled flasks), no solenoid nor needle valves, and ambient air entered through the MPV.



- **Operative ambient air measurements started on 27 Nov 2015.**
- **Target gas measurements started** on 18 Dec 2015 with a **7-hour cycle** (to monitor better the behaviour of the CRDS), which became a **21-hour cycle after 24 June 2016**.
- With the new plumbing configuration, **ambient air is alternatively sampled from the two inlet lines** within the 21-hour cycle (5 hours from general inlet and 15 hours from dedicated inlet).
- **Cooler bath temperature: -30 ºC**, therefore, **no complete drying**.

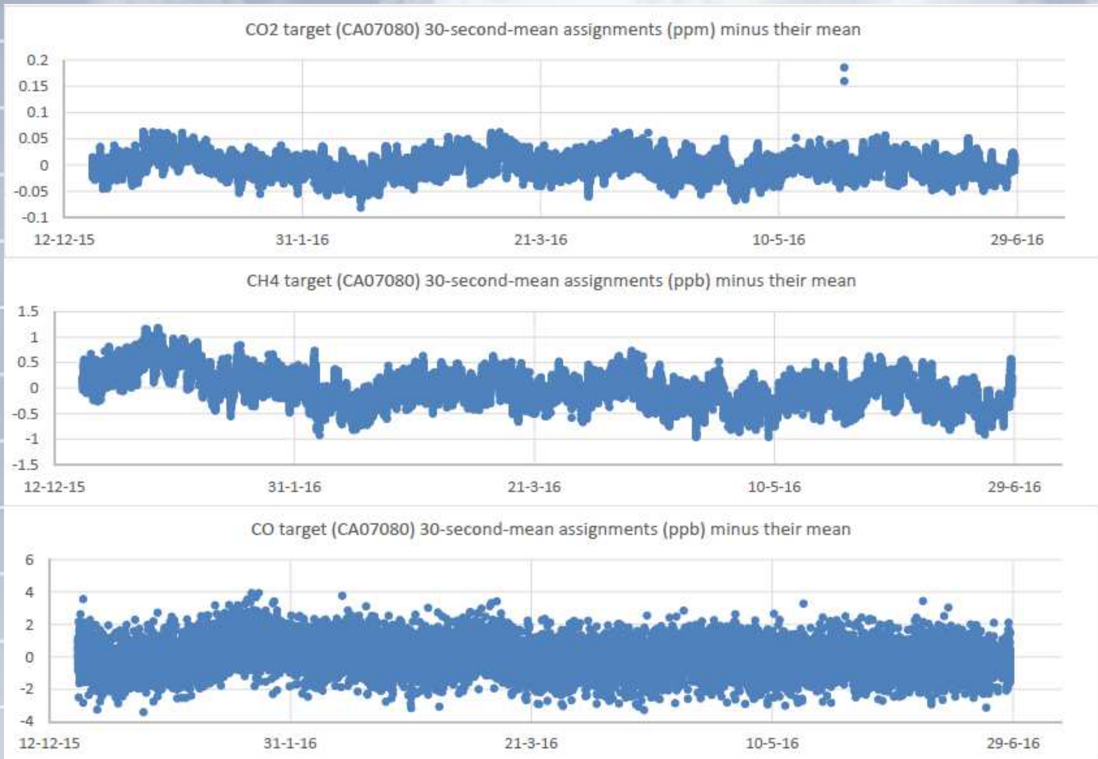
Ambient Air Measurement Processing

- The **processing software** has been **developed in Fortran 90** (there are some features and refinements that still need to be implemented).
- The **first step is computing raw-data 30-second means** using the DataLog_User files (no the syncronized ones), taking into account the "species" field (i.e., which fields have been updated in each file line; there are 1.7 lines/second).

- **For not discarding a 30-second mean**:
- **85%** of the expected **data** needs to be **present**.
- All the instantaneous data need to have the **same MPV position and solenoid valve configuration**.
- The **mean values** of the following variables **need to be within** the indicated ranges: cavity pressure, **140 +- 0.035 Torr**, cavity temperature, **45 +- 0.02 ºC**, and **outletvalve 20000-40000**.
- It needs to exit a calibration before and after the ambient mean considered, separated in time less than 180 days between them (as in ICOS).

- **Processing scheme**:
- Computation of the 30-second mean for the derived variable: peak84_spec_wet, and multiplication of this variable and CH4_raw by 1000.
- Aplication of the water vapour correction (dilution and pressure broadening effects).
- Aplication of the calibration curves interpolated linearly in time.

- This scheme is also used to assign mole fractions to the target and calibration gas injections, and it is checked that the water vapour correction for them is smaller than: 0.01 ppm for CO_2 and 0.1 ppb for CH_4 and CO.
- **Descarding due to stabilization time**: 10 minutes for ambient measurements, and 20 minutes for target and calibration gas injections.



GOBIERNO DE ESPAÑA | MINISTERIO DE AGRICULTURA Y PESCA, ALIMENTACIÓN Y MEDIO AMBIENTE | AEMet Agencia Estatal de Meteorología

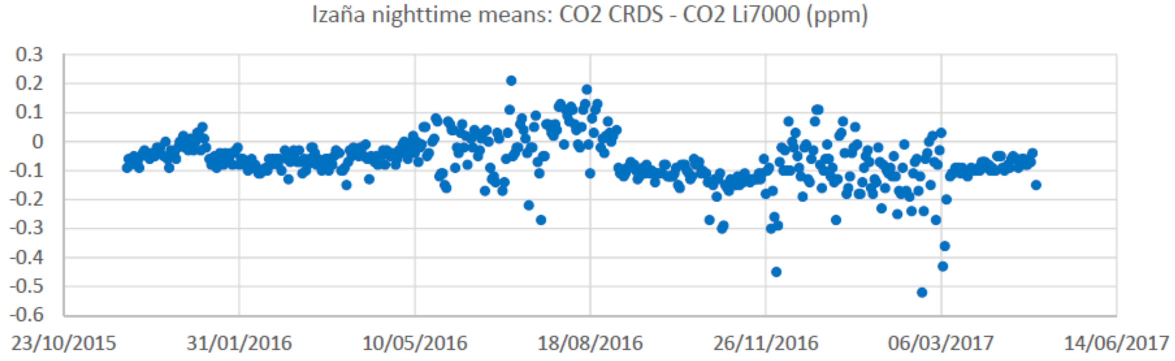
Target Gas Injections

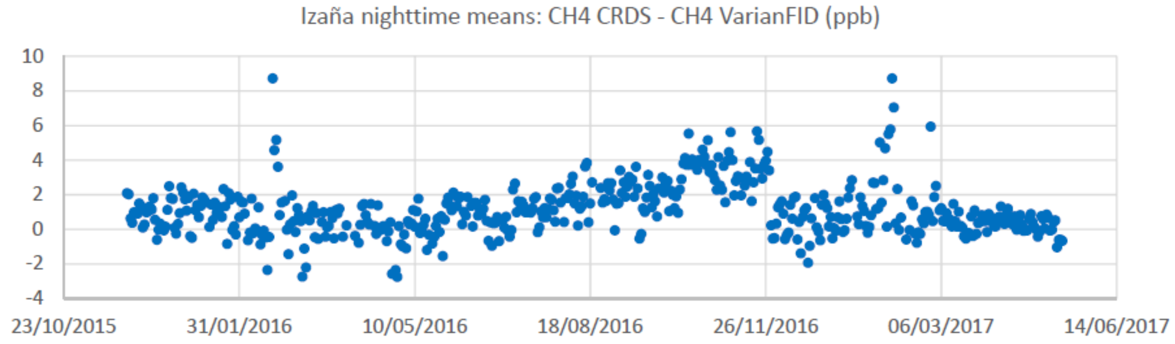
- 30-second-mean assignments to target gases.
- Good results.
- Note that 30-second is a too short time for CO, and it is necessary to consider longer averages for decreasing noise.

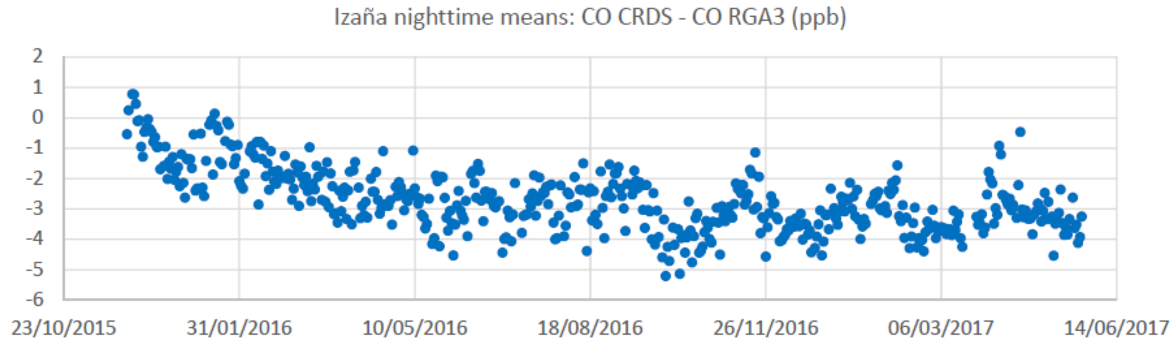
Tank/months	CO2 (ppm)	Std.Dev.	CH4 (ppb)	Std.Dev.	CO (ppb)	Std.Dev.
CA07080/ 7m	381.96	**0.020**	1825.43	**0.32**	148.60	**0.97**
CA05038/ 7m	368.85	**0.020**	1777.04	**0.33**	93.56	**0.99**
CA06812/ 13m	372.48	**0.020**	1784.80	**0.27**	142.04	**1.01**
CA05034/ 13m	363.71	**0.020**	1775.89	**0.27**	139.11	**0.98**

Comparison with other Izaña continuous measurements

- Comparison of **daily nighttime means** with other Izaña continuous measurements.
- **The data sets are still not final** and the origin of the discrepancies in some periods needs to be investigated.
- It seems **our set of CRDS laboratory standards** (WMO tertiaries) **might be drifting up significantly for CO** (increase of fit RMS, downdrift in targets, increase of the difference with RGA3). Maybe, there is also a small contribution from Primaries of the X2014A scale drifting less than initially computed by CCL.







Some additional novelties in the Izaña GHG instrumentation

- **Improvements introduced in the dedicated inlet lines**: 1) **back-pressure regulators** for the vents located downstream the pumps and rotameters for those vents; 2) **needle valves** in low flow vents installed downstream the cryotraps; 3) glass flask cryotraps with **Ultra-Torr connections**; 4) hermetic plugs for unused ports of the rotary Valco valves.

- **Preparation of two CO2 laboratory standards of 418.7 ppm for the Izaña NDIRs** Li7000 and Li6252 and calibration of them against our CRDS laboratory standards.

- **Reprocesing of the Izaña time series of CH4 and CO in the scales X2004A and X2014A**, respectively, taking into account also the drift of the 5 laboratory standards used in the Izaña RGA-3.

Thanks for your attention!

Teide Peak from Izaña Observatory
(Picture: Ángel J. Gómez-Peláez, Christmas 2016)