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

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Acquisition of a CRDS for CO_2, CH_4 and CO

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- 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

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- **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

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- **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 CO2 and CH4, 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 CO2, 1850 ppb of CH4 and 100 ppb of CO:

CO2	CH4	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

- **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**:

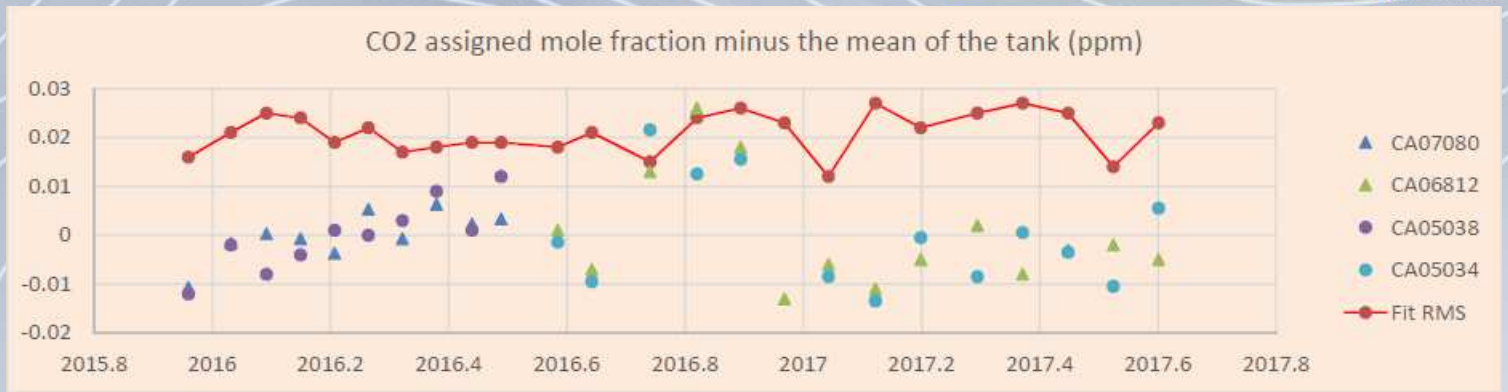
For CH4 and CO, a linear function:

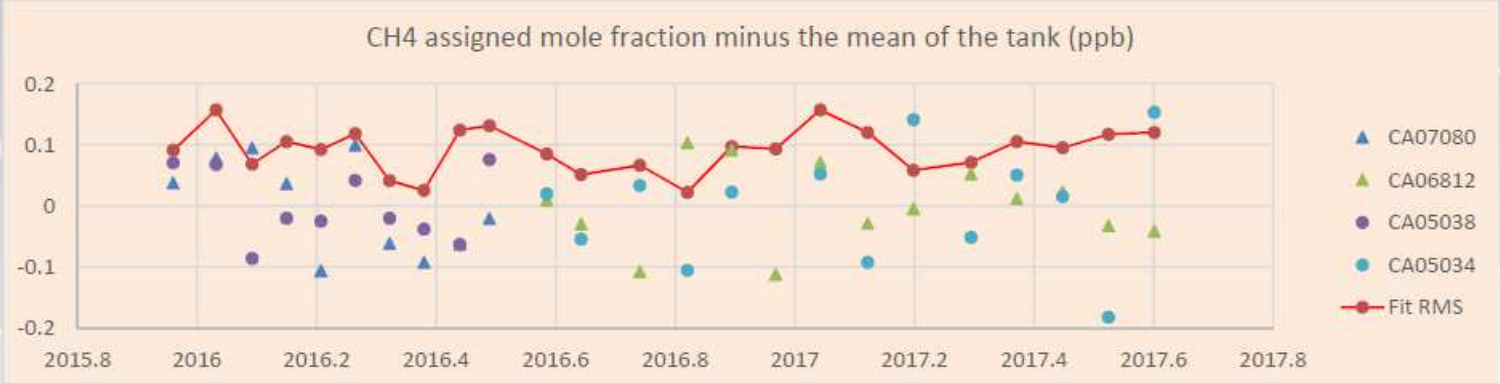
C_raw = a + b * C, where C is the real dry mole fraction (the gas standards are dry), and C_raw the raw signal.

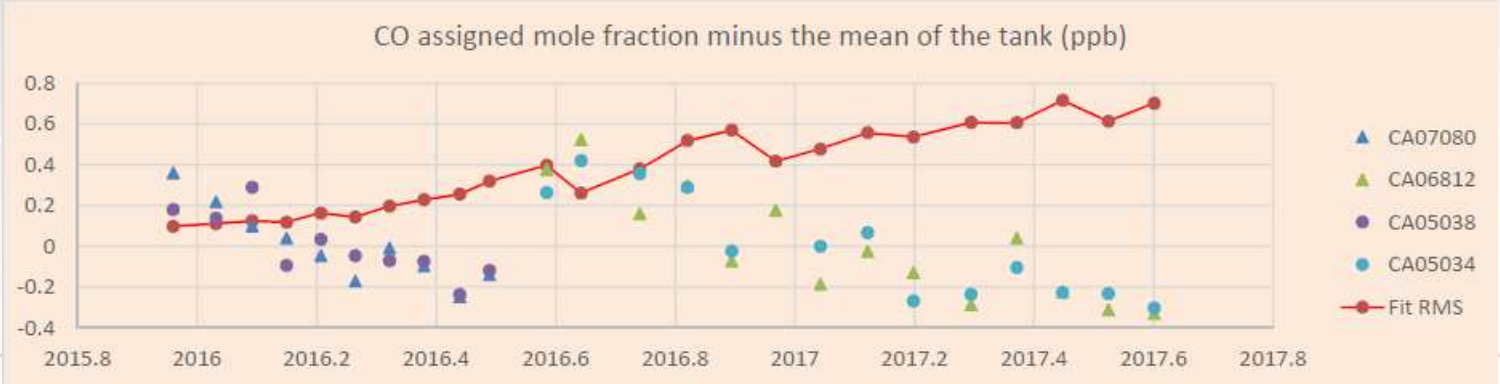
For CO2, a quadratic function with raw signal slightly corrected in outletvalve aperture (OV):

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

Calibration and Response Functions

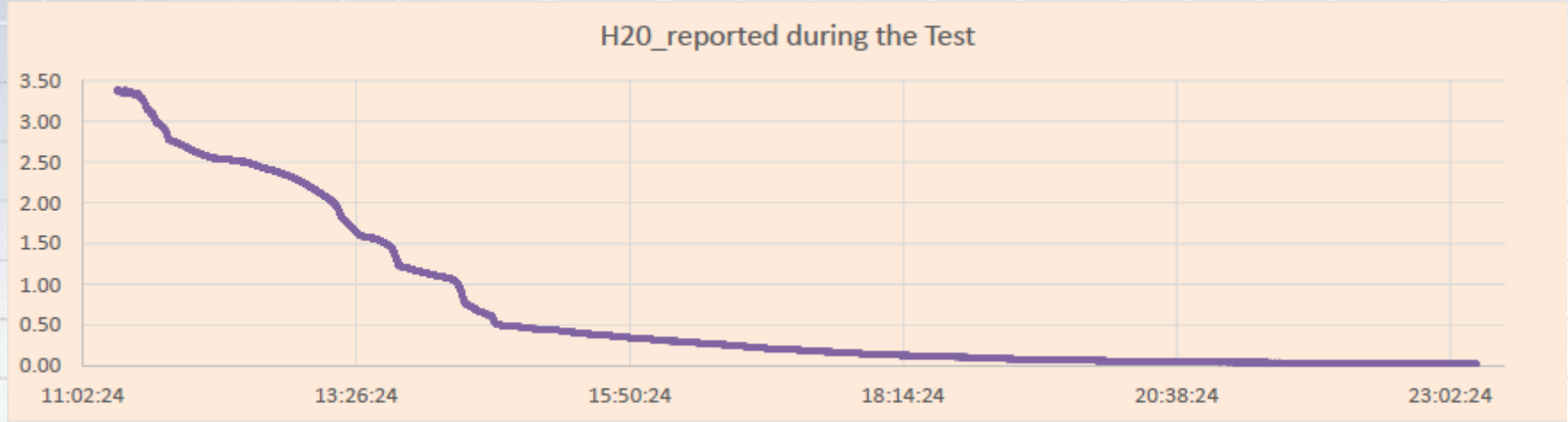






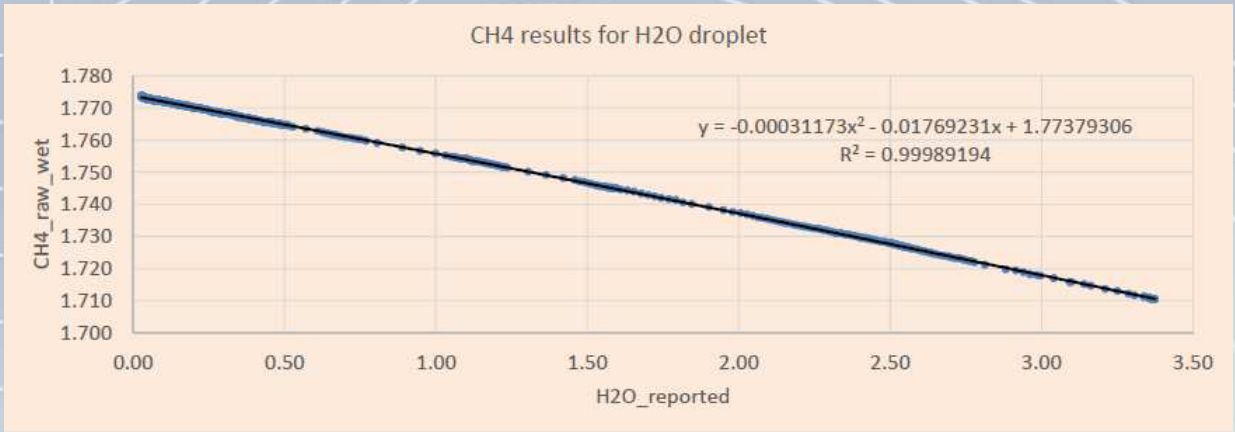
Water Vapour Correction: water droplet method

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



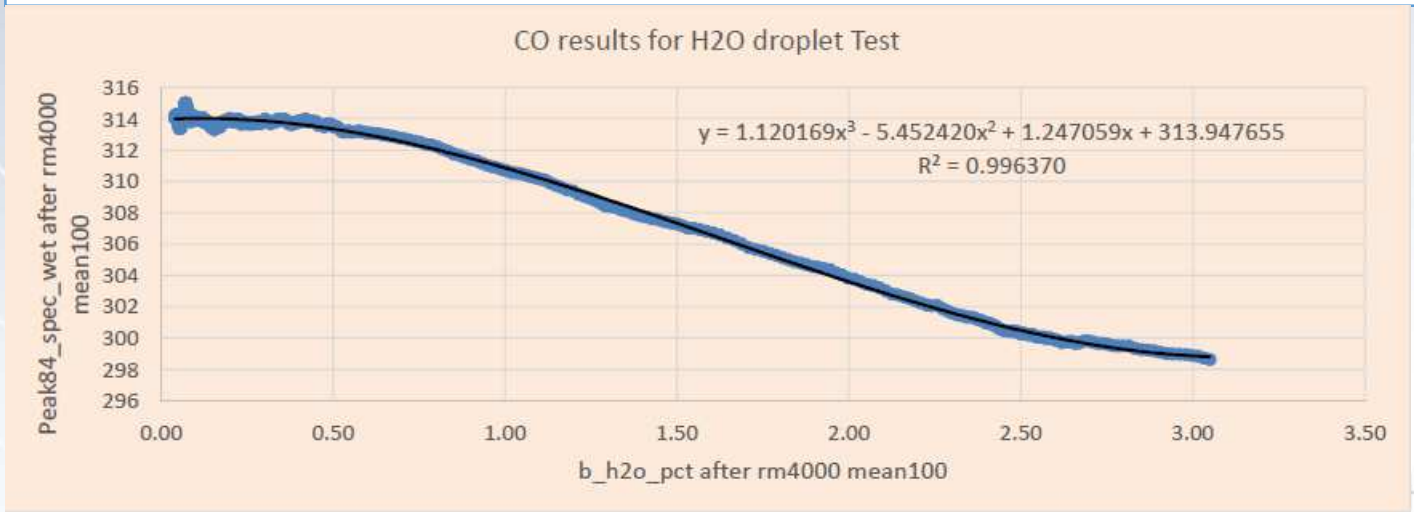
Water Vapour Correction: water droplet method

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



We use means of 100 instantaneous values for all the variables

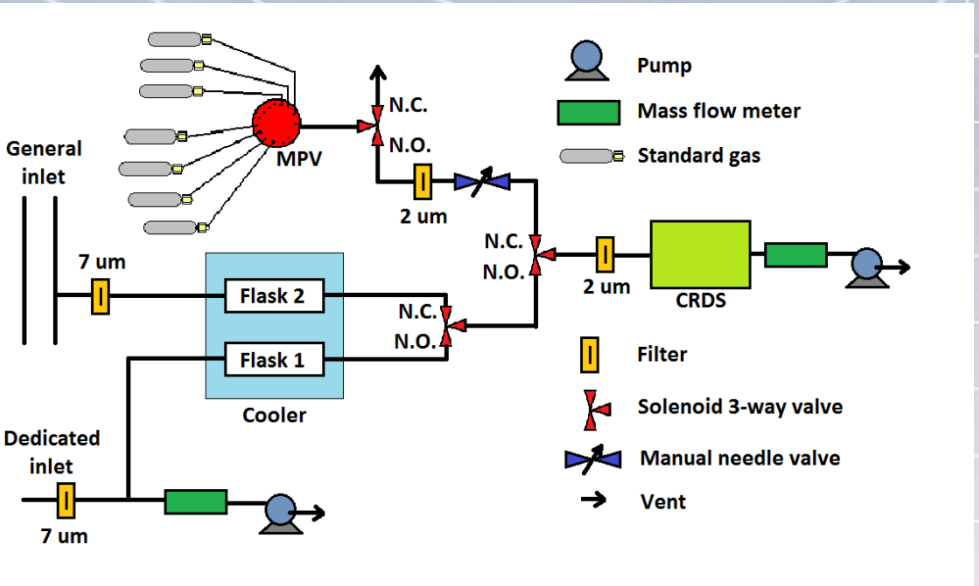
CO signal is very noisy, **but** the long duration of the experiment allows us using **4000-instantaneous-value running means** without compromising the accuracy of the data:



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

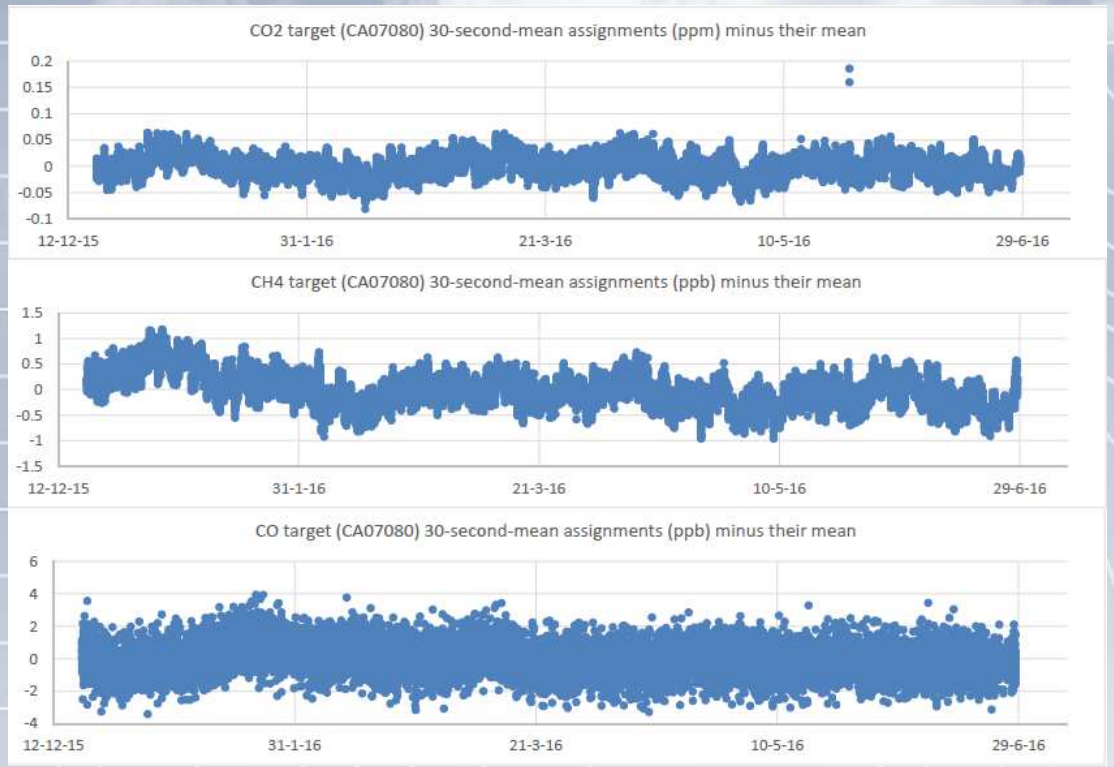
- The **processing software** has been **developed in Fortran 90** (there are some features and refinements that still need to be implemented).
- The **first step is computing raw-data 30-second means** using the DataLog_User files (no the syncronized ones), taking into account the "species" field (i.e.,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

Ambient Air Measurement Processing

- **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 CO2 and 0.1 ppb for CH4 and CO.
- **Descarding due to stabilization time**: 10 minutes for ambient measurements, and 20 minutes for target and calibration gas injections.



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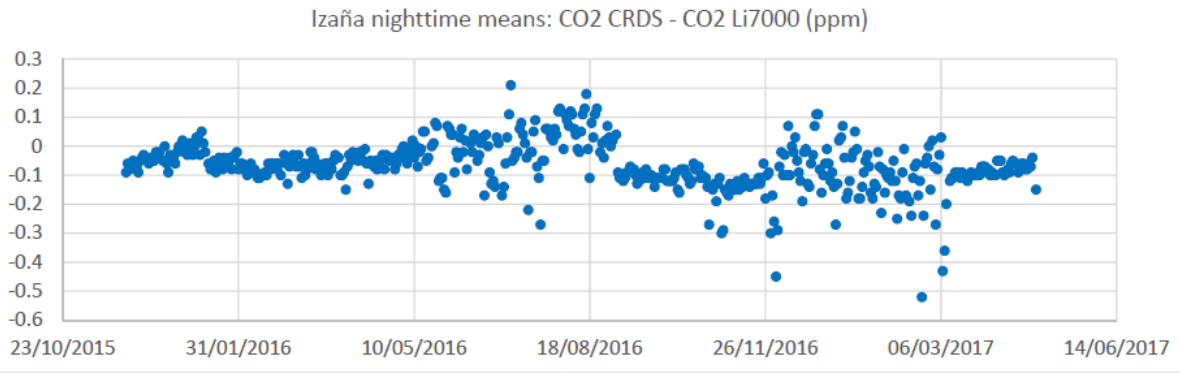
Target Gas Injections

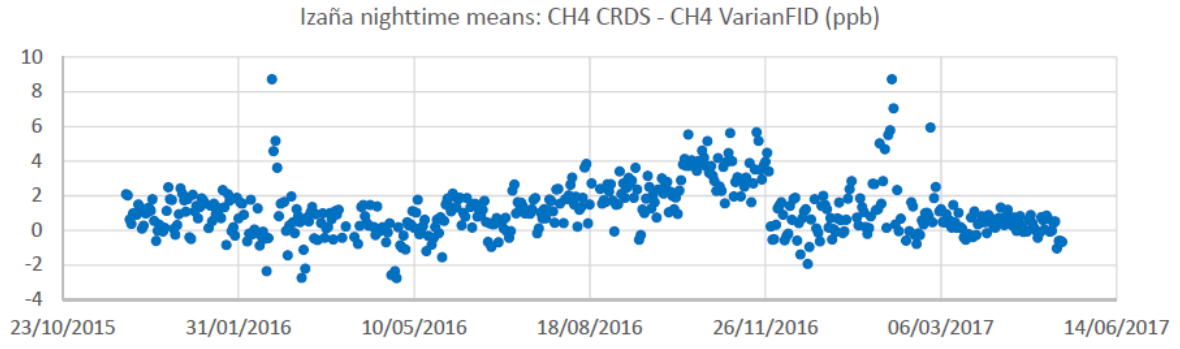
- 30-second-mean assignments to target gases.
- Good results.
- Note that 30-second is a too short time for CO, and it is necessary to consider longer averages for decreasing noise.

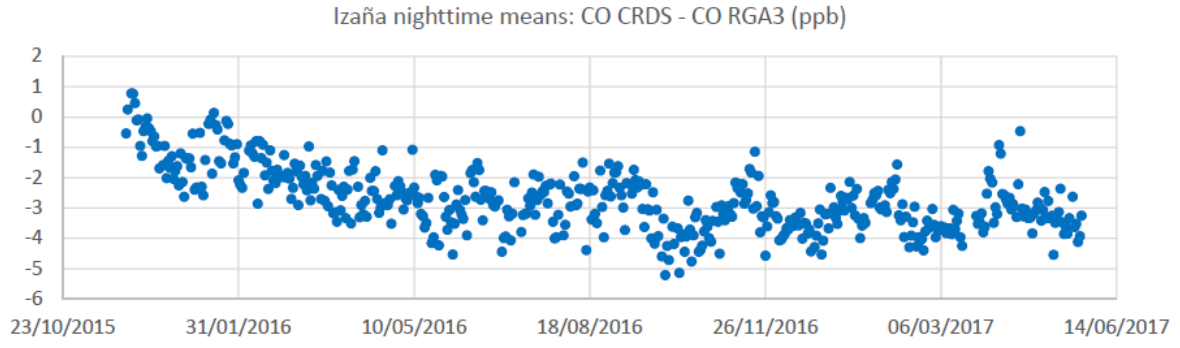
Tank/months	CO2 (ppm)	Std.Dev.	CH4 (ppb)	Std.Dev.	CO (ppb)	Std.Dev.
CA07080/ 7m	381.96	**0.020**	1825.43	**0.32**	148.60	**0.97**
CA05038/ 7m	368.85	**0.020**	1777.04	**0.33**	93.56	**0.99**
CA06812/ 13m	372.48	**0.020**	1784.80	**0.27**	142.04	**1.01**
CA05034/ 13m	363.71	**0.020**	1775.89	**0.27**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