In-situ CO measurements at Izaña global GAW station: GC-RGA system, data processing, and 2008-2011 time series

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Scheme of this talk:

1) Izaña station

2) System configuration

3) Response function, calibrations, and processing

4) CO time series analysis

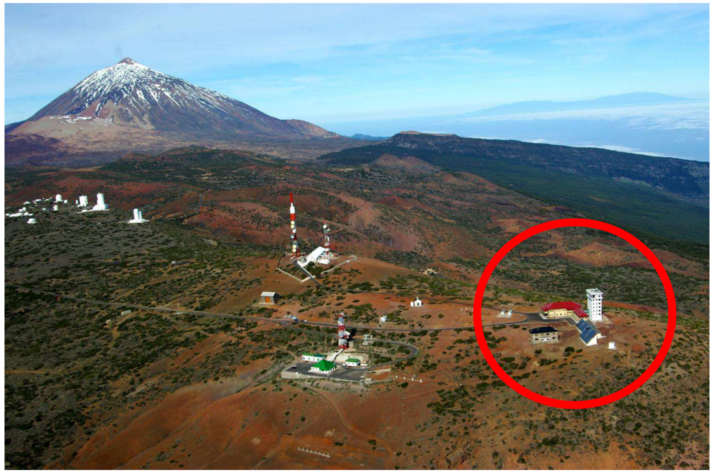
5) Estimation of standard uncertainty

6) Flasks-Continuous comparison, uncertainty, and weighted means

This work intended to be a peer review paper for the AMT GGMT special issue

Izaña Atmospheric Observatory:

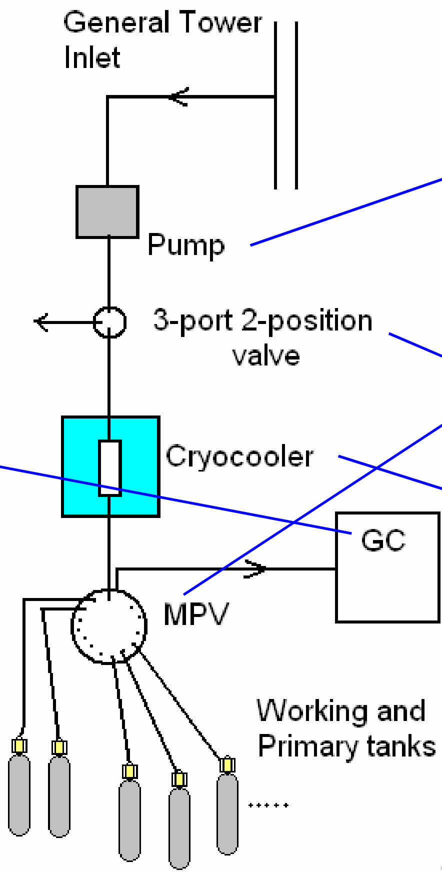
- Global GAW Station,
- NDACC Station, ...

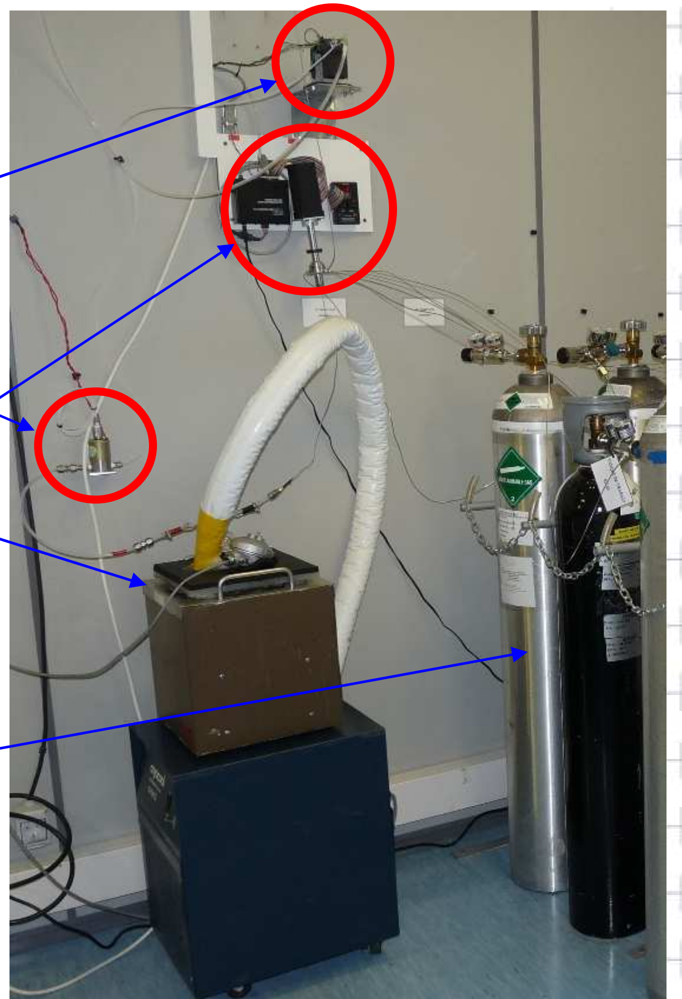


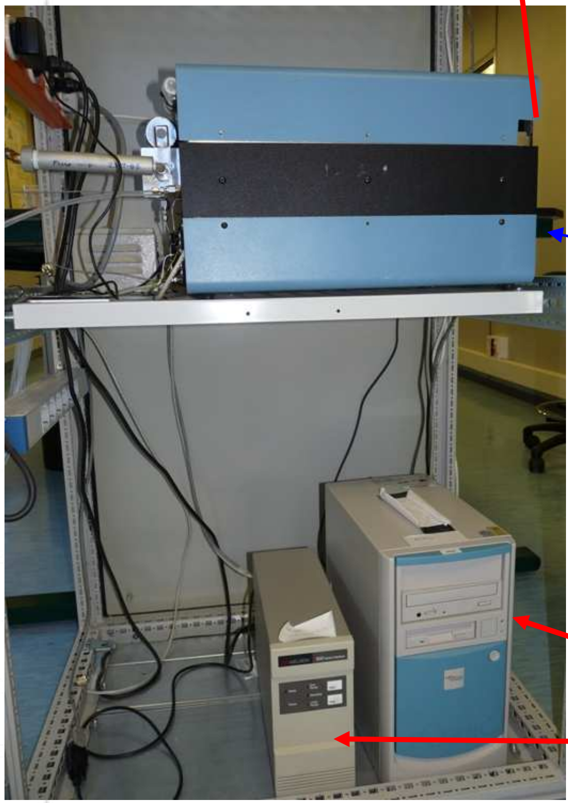
Measurement system scheme:

GC-RGA3 (Reduction Gas Analyzer)

Sampling/selection system scheme:







PC

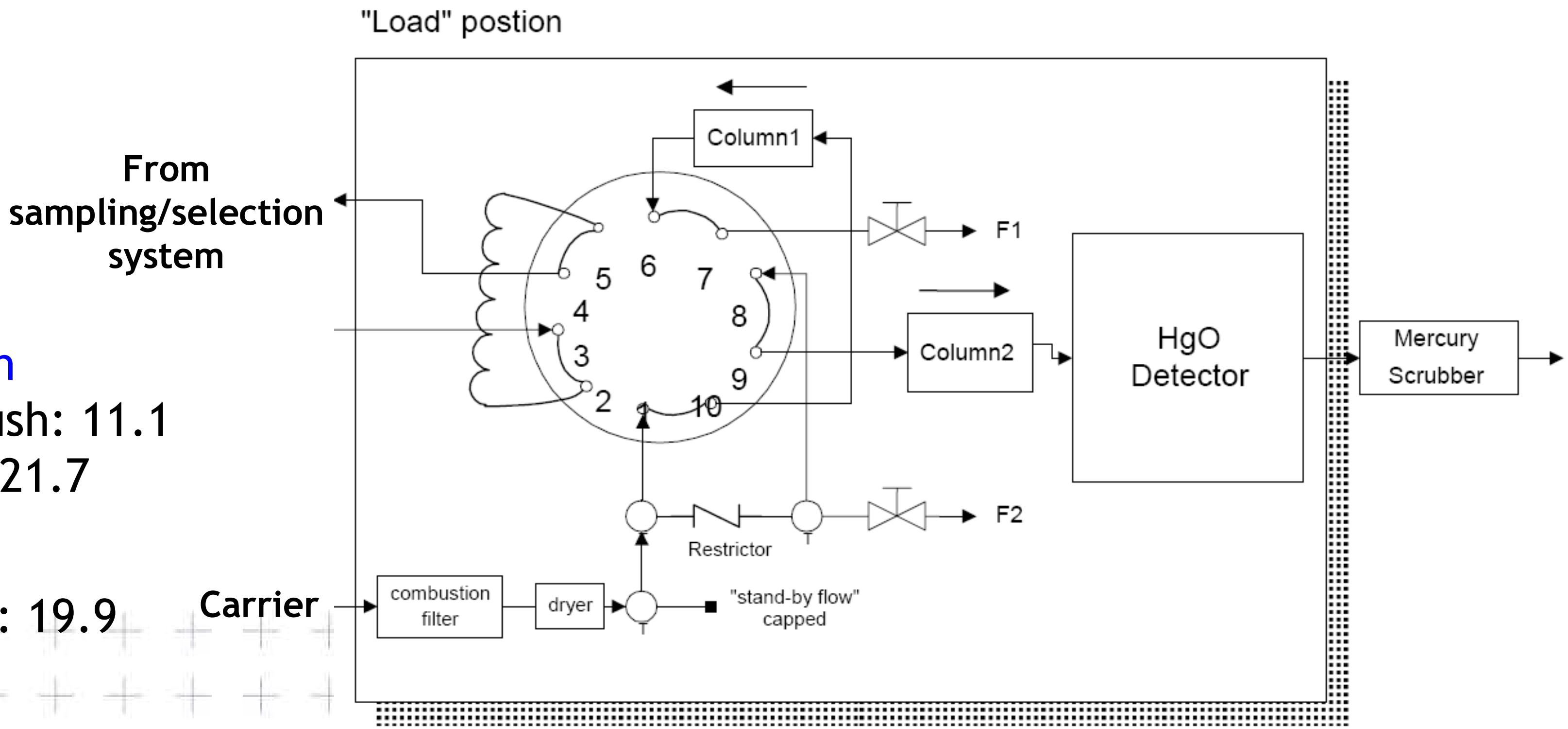
Integrator

Modified internal configuration of the GC-RGA3:

- Two-positions ten-ports injection valve (positions: load/backflush, inject). Loop size: 1 ml
- Two chromatographic columns (pre-column (1): Unibeads 1S 60/80; main column (2): Molesieve 5A 60/80)
- Carrier gas: synthetic air (traps: Sofnocat and Molesieve)
- Temperatures. RGA: 265 °C. Columns oven: 105 °C

Carrier flows:

- Load/Backflush position. Backflush: 11.1 ml/min. Direct: 21.7 ml/min
- Inject position: 19.9 ml/min

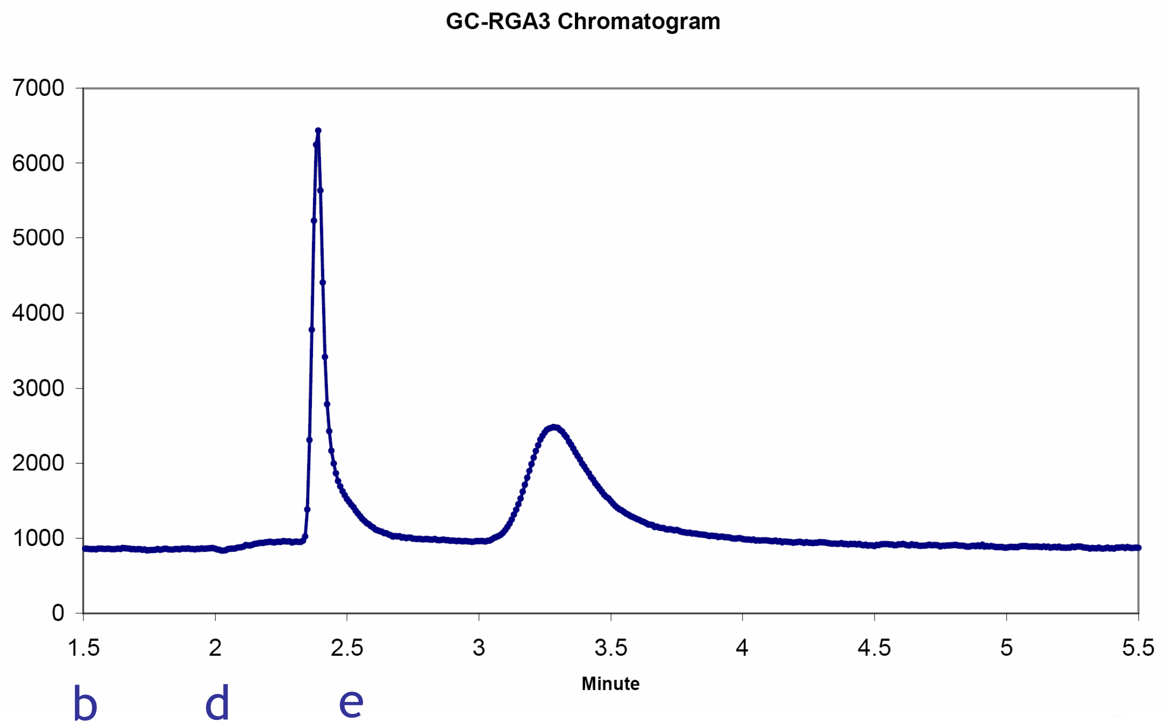


Ambient air injection sequence:

20 minutes cycle with two 10 minutes subcycles.

- First: working gas
- Second: ambient air

[*] Sample loop flushing with ambient air has a larger flow rate than for the standards (working or Lab) and starts 5 minutes before.



Time sequence for the 10 minutes subcycle (valid calibrations and ambient air mode):

Time (min)	Label	Description
00:00	a	Start of sample loop flushing(100 ml/min)[*]. Electronic zero.
01:30	b	Start of chromatogram adquisition
01:55	c	End of sample loop flushing. Start of pressure equilibration.
02:00	d	Injection valve goes from “Load” to “Inject”
02:30	e	Injection valve goes from “Inject” to “Load”

Response function and calibrations:

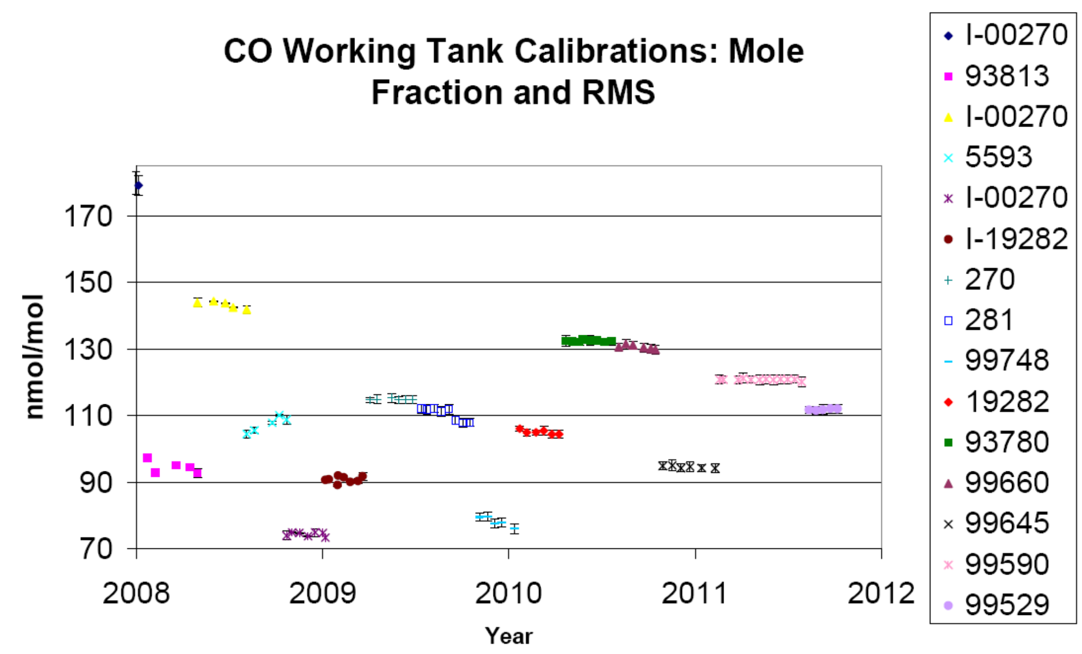
$$r = r_{wt}(h/h_{wt})^b$$

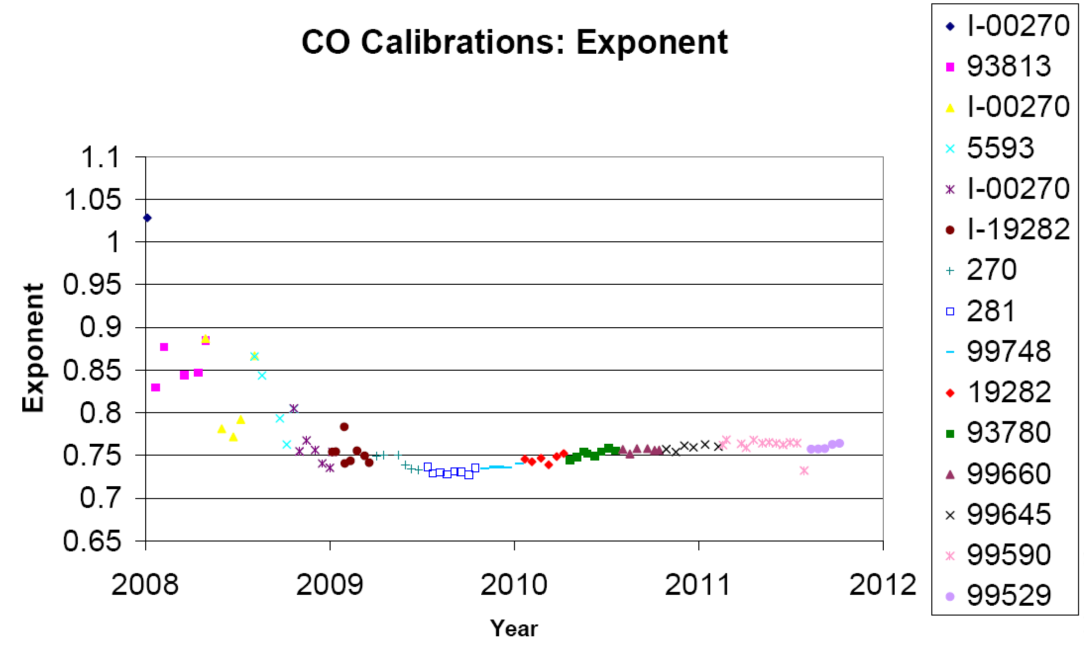
Exponent (b) and working gas mixing ratio (r_{wt}) are obtained in the **calibrations**, which are carried out every 2 weeks, using between 3 and 5 WMO standard gases (5 levels since March 2009)

- Lifetime of a work tank: between 3 and 5 months
- Calibration scheme since March 2009. 5 cycles. Cycle: wt-s1-s2-wt-st3-st4-st5
- We have created a Fortran 90 code to process calibrations (with this and other types of cycles used in the past)
- h/h_{wt} is computed interpolating the heights of bracketing wt injections
- It is possible to discard single outlayer injections
- Mean h/h_{wt} and sample standard deviation are computed for each standard level
- Coefficients. Least-squares fitting to the function $\ln r = \ln r_{wt} + b\ln(h/h_{wt})$
- The Root Mean Square (RMS) of the residuals is computed as:

$$RMS = \sqrt{\sum_i (r_i - R(h_i/h_{wt}))^2 / (n-2)}$$

where ***n*** is the number of standard levels, and $R(h/h_{wt})$ is the response function





The **time dependent GC-RGA response function**, for the working gas in use, is computed from the response functions determined in its calibrations:

- *b* is computed as the mean of the calibration values

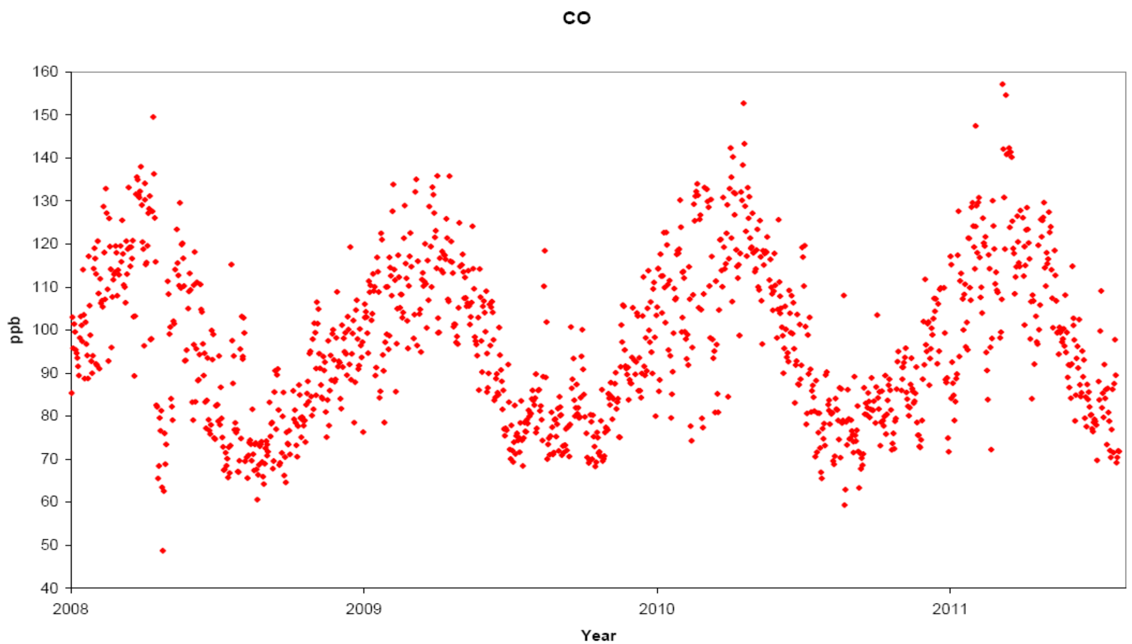
- A linear drift in time is allowed for r_{wt} (Snedecor's F tests are used, as described by Gomez-Pelaez & Ramos 2011).

Once the time dependent GC-RGA response function is known, ambient data processing can be done with a Fortran 90 code.

Discarding of outliers is done in a similar way as in Gomez-Pelaez et al. (2006) for CH_4:

- firstly for the h_{wt}/r_{wt} time series (with thresholds $5\sigma, 4\sigma, 3.5\sigma$ from the running means of 7, 2, and 0.19 days, respectively)

- then for the ambient air mole fraction series (with thresholds $4.5\sigma, 4\sigma, 3.5\sigma$ from the running means of 30, 3, and 0.26 days, respectively)

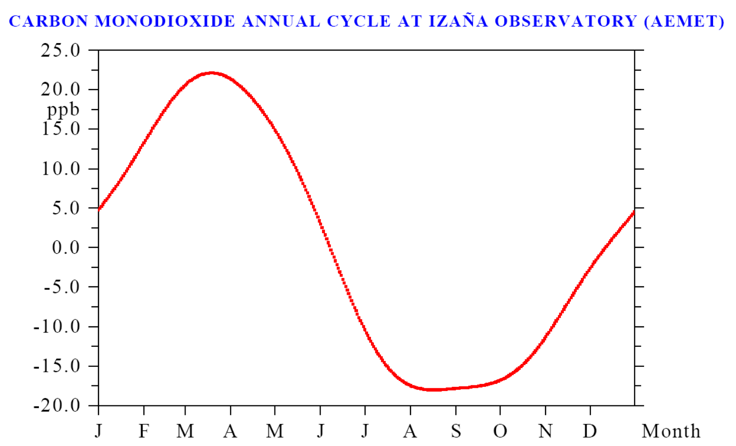


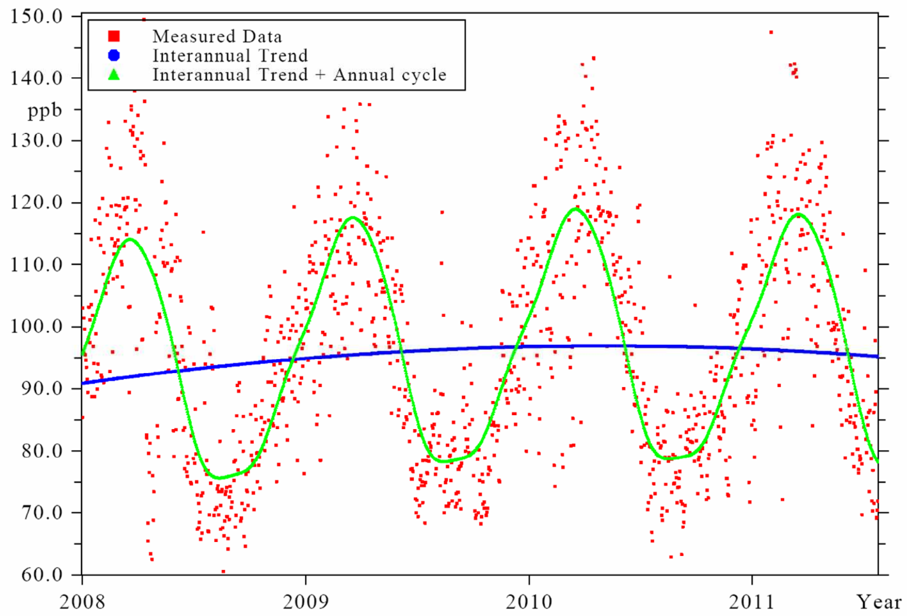
Daily night mean CO time series

CO time series analysis:

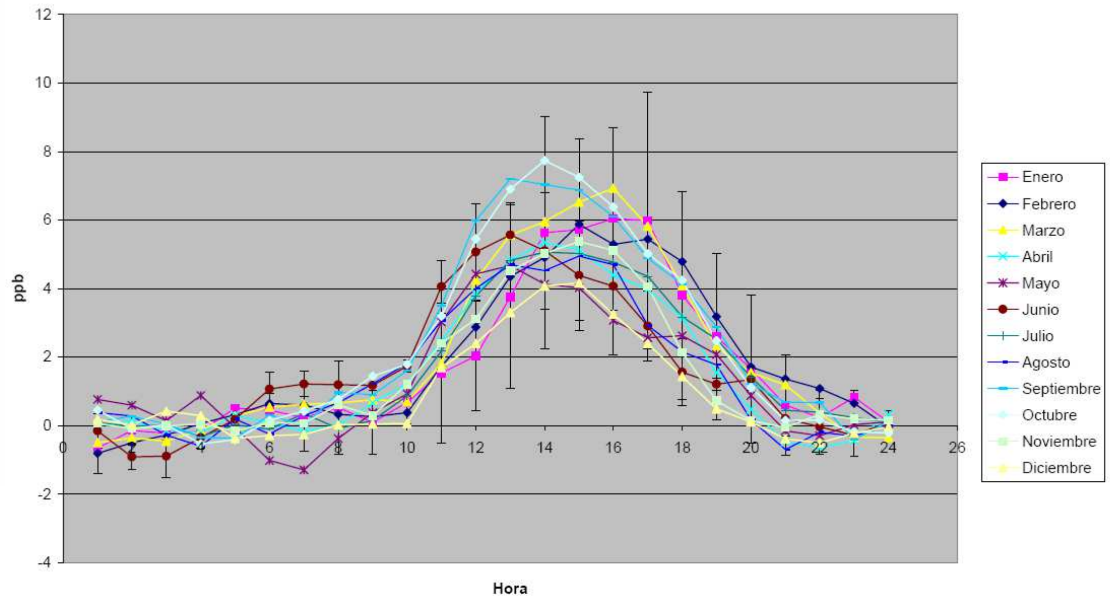
Daily night mean CO fitting:
Interannual trend (2nd order polynomium) + Annual cycle (4 Fourier harmonics)

- 3.5 years of data: harmonics are not needed for the interannual trend
- Assumption: the same annual cycle for all the years





CO daily cycle relative to nocturnal background conditions (2009-2011)



Estimating "internal" standard uncertainty:

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Response function: $r = r_{wt}\left(h / h_{wt}\right)^{b}$, internal standard uncertainty:

$$\sqrt{(RMS)^2 + \left(\frac{r}{r_{wt}}\sigma_{r_{wt}}\right)^2 + \left(b \cdot r \frac{h_{wt}}{h}\frac{\sigma_{h/h_{wt}}}{\sqrt{3}}\right)^2 + \left(r\left[\ln\frac{h}{h_{wt}}\right]\sigma_b\right)^2}$$

(1) (2) (3) (4)

Origin of the standard uncertainty components:

(1) Consistency between the laboratory standards and the response function (RMS)

(2) Consistence of the work gas mole fraction along its lifetime (ConsisWT)

(3) Repeatability of relative height for hourly means (Repeat_hrel)

(4) Uncertainty in the exponent (UncerExp)

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Typical values of the uncertainty components and combined uncertainty:

(ppb) ⟶	RMS	ConsisWT	Repeat_hrel	UncerExp	Combined
2008	0.8	0.92	0.27	0.53	1.41
2009-2011	1.1	0.56	0.25	0.09	1.27

These are estimated typical values. Indeed, the combined uncertainty and its components can be estimated for each ambient air injection, so having a time series for each uncertainty component.

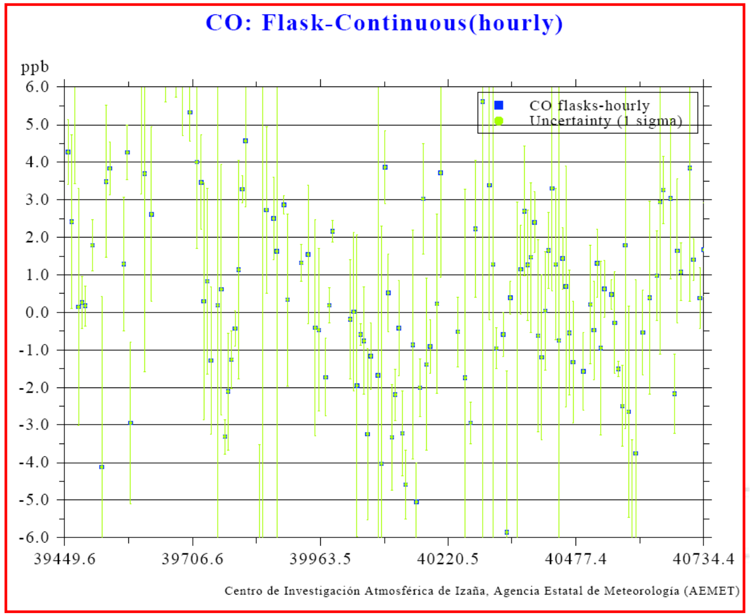
Continuous in-situ hourly means versus NOAA weekly flasks:

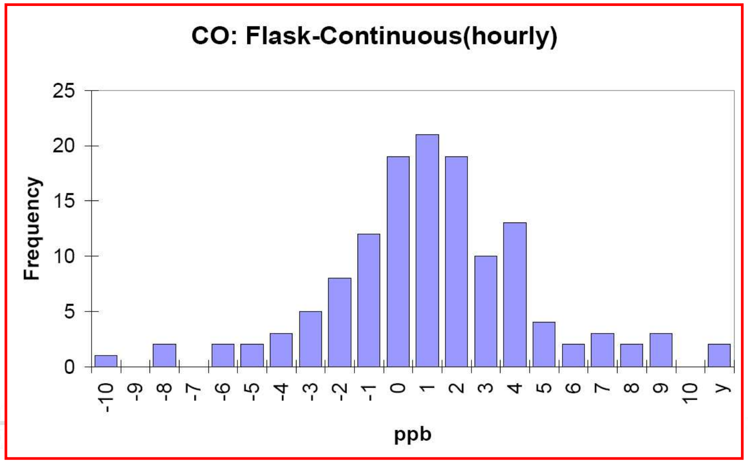
Fortran90 code to compare in-situ continuous hourly means with NOAA flasks. The comparison has the following **novel characteristics**:

1. Flasks only are accepted if have **flags** "…" or "..P", and both members of the pair are present. $r_{f1}, r_{f2} \Rightarrow \bar{r}_f, \sigma_f = \left| r_{f2} - r_{f1} \right| / \sqrt{2}$

2. Each pair is compared with the hourly mean (r_c) simultaneous in time (the hourly mean time interval must contain the time of the pair sampling).

$dif = \bar{r}_f - r_c \ , \qquad \sigma_{dif} = \sqrt{\sigma_f^2 + \sigma_c^2}$ "internal" standard uncertainty of the difference





3. Global and annual difference means and standard deviations are computed using 3 types of means (and standard deviations):

- ***Mean*** is the conventional mean.

- ***FWMean*** is a "full" weighted mean computed following the minimum variance method (maximum likelihood for Gaussian distributions).

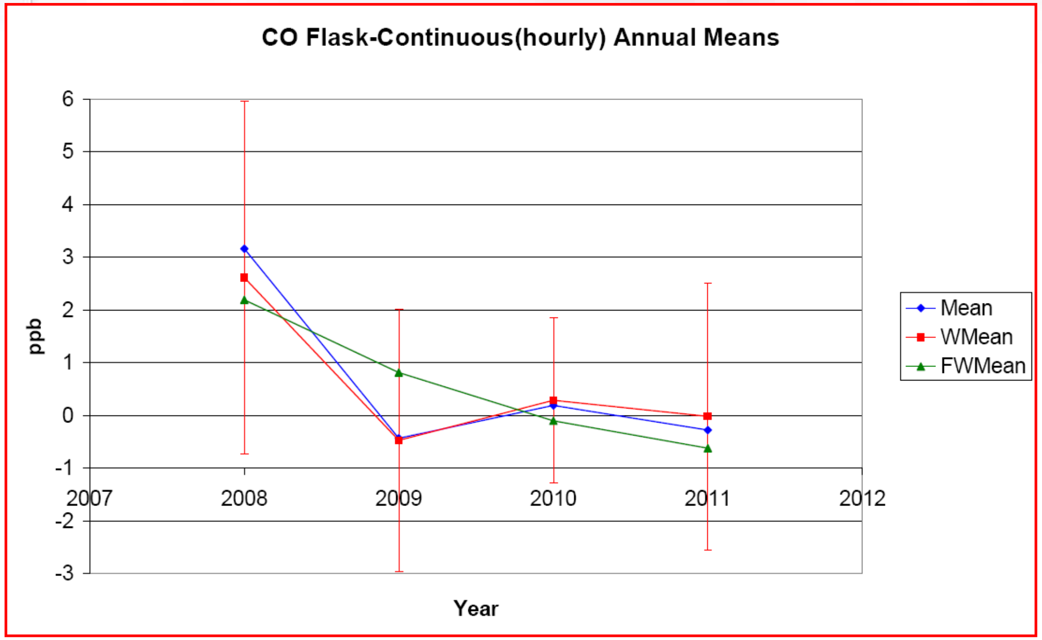
$$< dif >_{FW} = \left(\sigma^2_{inv} / n\right) \sum_{i=1}^{n} dif_i / \sigma^2_{dif\ i} \quad \text{with} \quad n / \sigma^2_{inv} = \sum_{i=1}^{n} 1 / \sigma^2_{dif\ i}$$

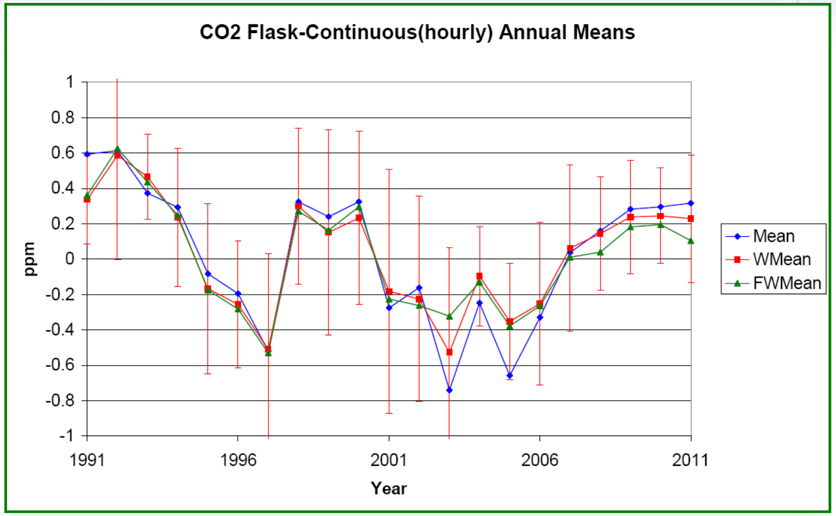
- ***WMean*** is an "intermediate" weighted mean. The same equations apply but $\sigma_{dif\ i}$ is replaced by the median of σ_{dif} for those $\sigma_{dif\ i}$ smaller that the median of σ_{dif}

The basic idea: differences with a larger uncertainty provide information of a lower quality to compute de mean.

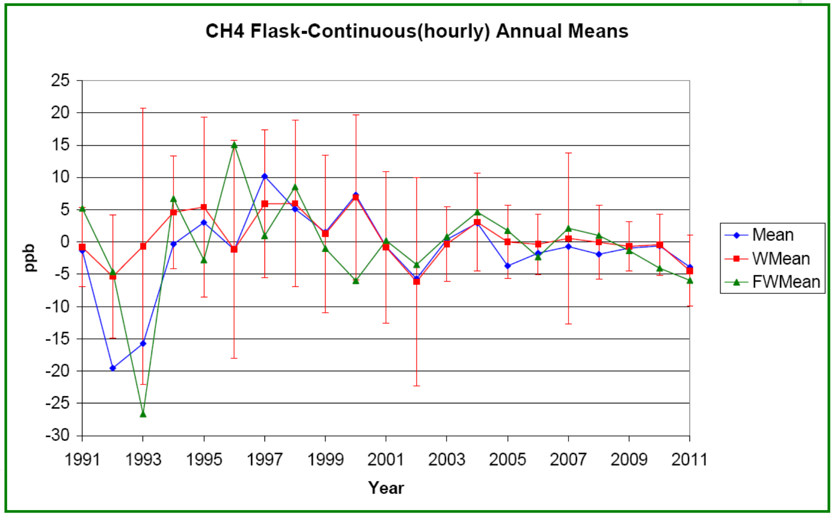
Means and their standard deviations have the following values:

Mean	Est.dev.	WMean	Est.dev.	FWMean	Est.dev.
0.82	5.36	0.65	2.81	0.64	2.46



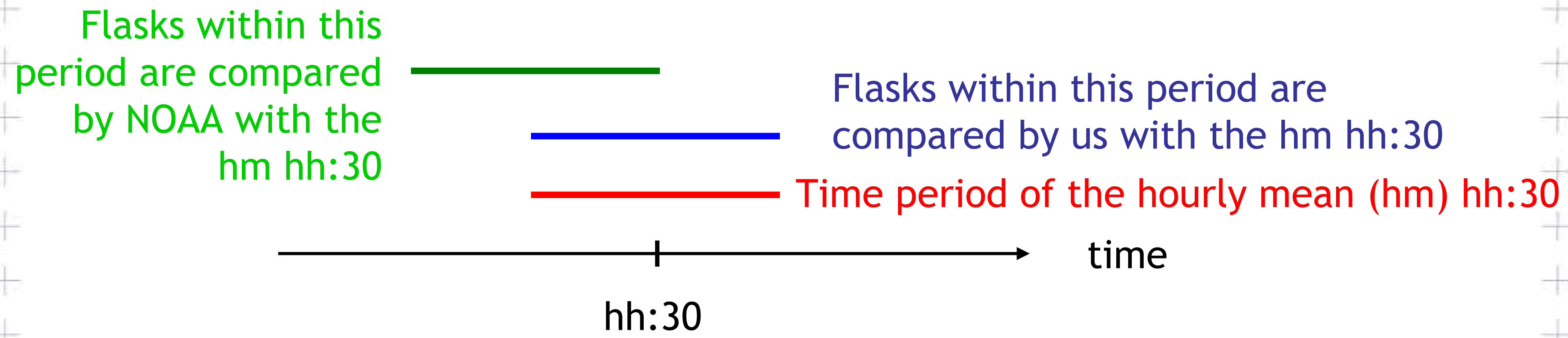


CO comparison results for 2009-2011 are much better that those for 2008.



Which are the differences with NOAA's software for flasks-continuous comparison:

- More accurate time correspondence (so, do not rely on time persistence)



- Rejection of flasks with flags: ".X." and ".XP". Non-background conditions means larger internal variability and larger uncertainty.
- For CO_2 at Izaña, we get smaller departures from zero of the anual conventional means (because the differences have smaller random and systematic "noise")
- The uncertainty of the differences is computed
- Weighted means based on uncertainty are used

Thank you for your attention !