

New improvements in the Izaña (Tenerife, Spain) global GAW station in-situ greenhouse gases measurement program

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Abstract

We present the main improvements in the in-situ Izaña (Global GAW station) greenhouse gases (GHGs) measurement program during the last few years. First, we present the calibration schemes for the GC-ECD used to measure atmospheric N₂O and SF₆, their calibration processing and statistics, and the software developed for ambient data processing taking into account the hierarchy of calibrations. Also, the in-situ Izaña N₂O and SF₆ series (from June 2007 till July 2011) are showed. Second, we present the software developed to compare in-situ Izaña GHG measurements with co-located NOAA flasks, and summarize the results of such comparisons for CO₂, CH₄, N₂O and SF₆. Third, some novelties concerning the in-situ Izaña CH₄ measurements are detailed, and its time series is updated. Finally, the update of the Izaña in-situ CO₂ time series is showed.

1. N₂O and SF₆ calibration and ambient data processing

Izaña's N₂O measurement program passed satisfactorily a scientific audit carried out by WCC-N₂O in November 2008; see Scheel (2009). Gomez-Pelaez & Ramos (2009) describe the system to measure N₂O and SF₆ at Izaña station (GC-ECD system configuration, time sequences, and chromatograms), but there have been some changes: 1) We have changed the method for locating peak baselines, considering SF₆ as a tangent peak far on the tail of the N₂O peak (instead of forcing a valley baseline), and have reintegrated the full series of chromatograms; 2) The one hour injection cycle for ambient air measurements described in Table 2 of that reference was in operation till November 3, 2008. Since such date, the injection cycle lasts 15 minutes: working gas (minute 00:00), and ambient air (minute 07:30); 3) The calibration basic cycle was changed on November 3, 2008. Before such date, it was st1-st2-st3-st4-st5-wt1-wt2-wt1; after that date, it has been wt-st1-wt-st2-wt-st3-wt-st4-wt-st5; where wt indicates working gas, and st indicates standard gas.

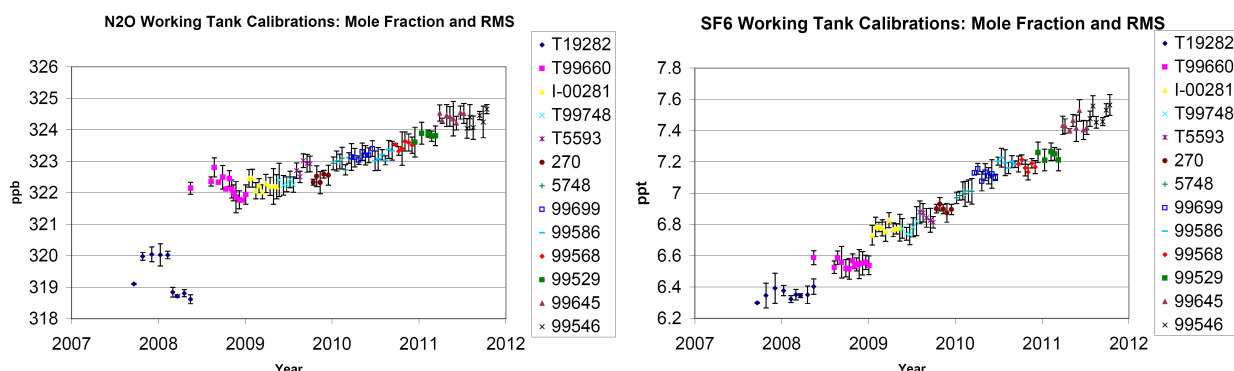


Figure 1. Left and right graphics show working gas mole fractions determined in the calibrations for N₂O and SF₆, respectively; and the RMS (as error bars) of the fitting residuals (taking into account the effective number of degrees of freedom).

We work with the ratio h/h_{wt} : peak height relative to working gas peak height (interpolating bracketing working gas injections). The *response function* used assumes that h/h_{wt} is a quadratic polynomial in N₂O mole fraction, and a linear polynomial in SF₆ mole fraction. Calibrations are carried out every 2 weeks. Processing them, response functions, working gas mole fractions, and uncertainties are obtained.

We have developed Fortran90 numerical codes to process calibrations, and ambient data, taking into account the hierarchy of calibrations. We sketch briefly such processing. Each calibration has 5 cycles. Mean h/h_{wt} and sample standard deviation are computed for each standard level. The coefficients of the response function are obtained through least-squares fitting to the h/h_{wt} means. Once the coefficients are known, the N_2O response function is rewritten as:

$$h/h_{wt} = 1 + slope(r - r_{wt}) + a_2(r - r_{wt})^2 \quad (1),$$

where $slope = a_1 + 2a_2r_{wt}$, r_{wt} is the working gas mole fraction (the solution of the response function for $h/h_{wt}=1$), and a_0 , a_1 , and a_2 are the coefficients of the quadratic polynomial, being the sub-index the power of the accompanying mole fraction in the polynomial. For SF_6 , equation (1) is used too, but with $a_2=0$. Figure 1 shows the r_{wt} determined in the calibrations, and the RMS (as error bars) of the fitting residuals, where the Mean Square is computed as the square residuals summatory divided by 2 or by 3 (for N_2O or SF_6 , respectively), the effective number of degrees of freedom (instead of 5, the standard levels).

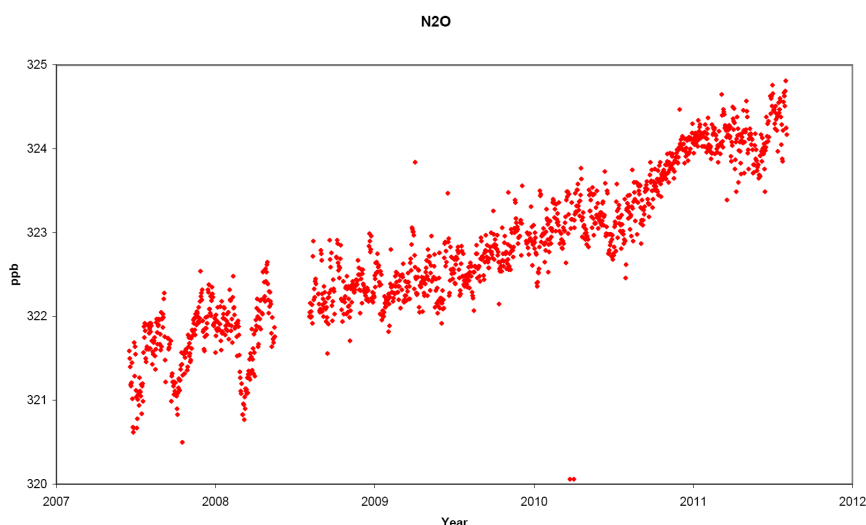


Figure 2. Izaña in-situ measured N_2O daily night mean (20:00-08:00 UTC).

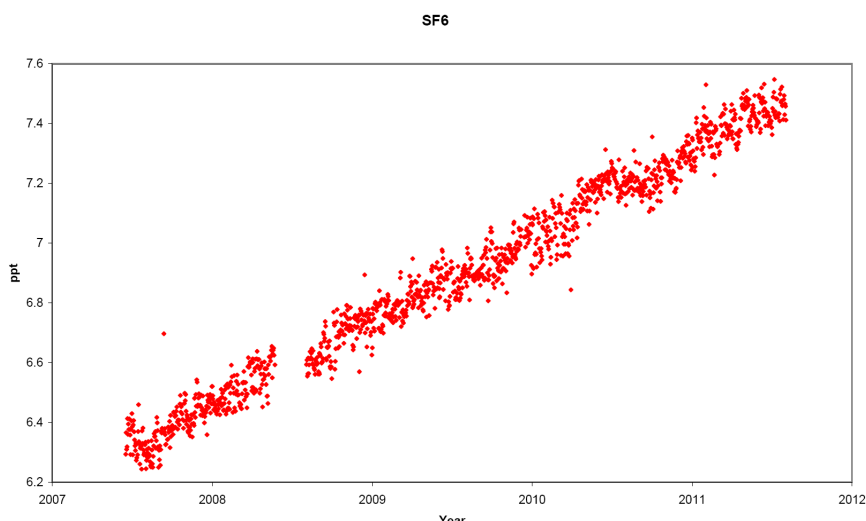


Figure 3. Izaña in-situ measured SF_6 daily night mean (20:00-08:00 UTC).

The time dependent GC-ECD response function, for the working gas in use, is computed from the response functions determined in the calibrations. For SF_6 , r_{wt} and $slope$ are computed as the mean of the values obtained in the calibrations. For N_2O , $slope$ and a_2 are computed as the mean of the calibration values; whereas a linear drift in time is allowed for r_{wt} (Snedecor's F

tests are used, as described by Gomez-Pelaez & Ramos 2011, but with a 95% confidence level).

For ambient measurements, *discarding of outliers* is done in a similar way as in Gomez-Pelaez et al. (2006) for CH₄; firstly for the h_{wt}/r_{wt} time series, and finally for the ambient air mole fraction series. *Dilution correction is applied for N₂O* (see below, the second paragraph of the section “Novelties in the CH₄ program, and time series update” of this report). A *correction, due to a small bias produced by the ambient air inlet line, is applied to N₂O mole fraction*. Such bias has been *accurately determined using 8 working tanks filled with ambient air at Izaña station*. The physical reason of the bias is being investigated.

2. Comparison between flasks and continuous measurements for CO₂, CH₄, N₂O and SF₆

We have developed a Fortran90 numerical code to compare in-situ continuous measurements with simultaneous collocated NOAA flask samples. The inputs of the programme are hourly mean in-situ data files (in the old WDCGG format) and a NOAA flask data file (NOAA format).

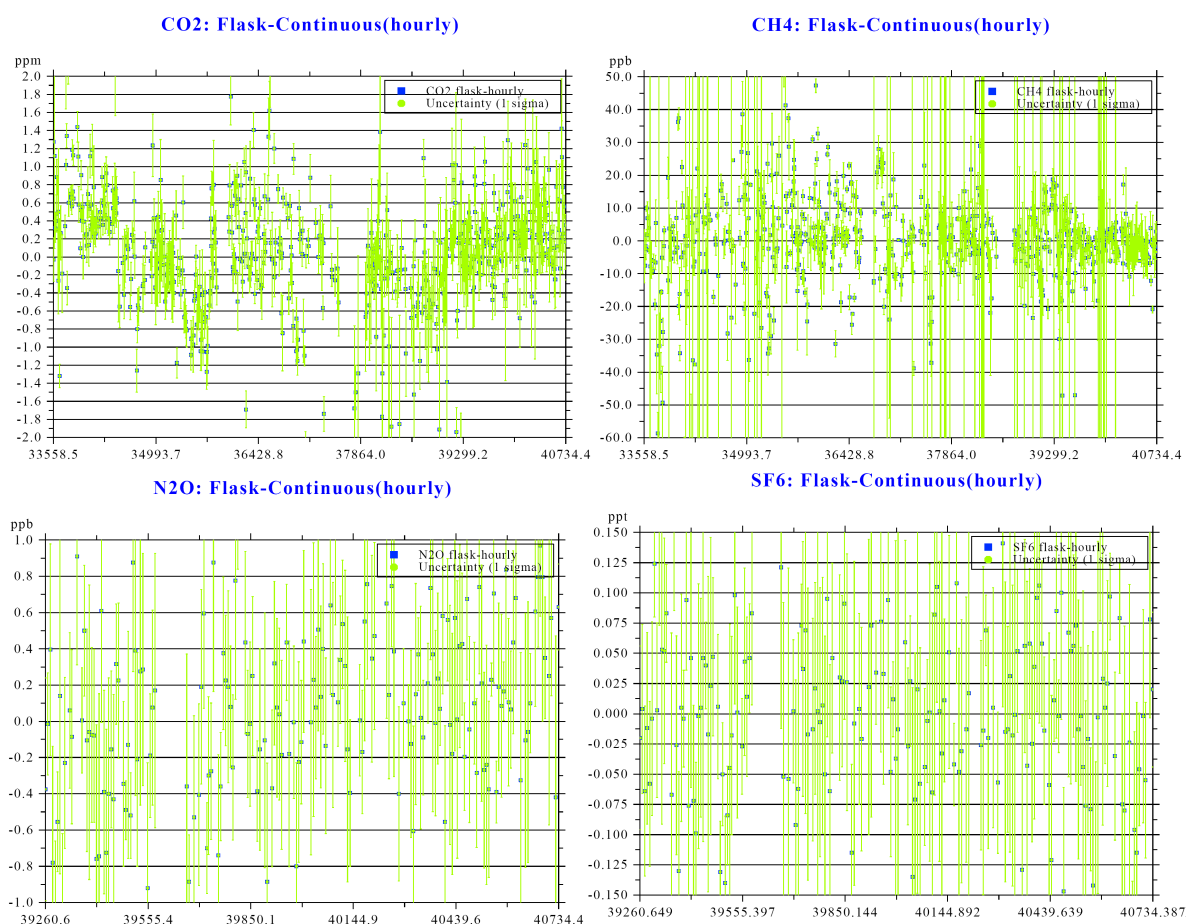


Figure 4. Flask minus continuous difference time series for CO₂, CH₄, N₂O, and SF₆, and internal standard uncertainty. When there is only one available injection for the hourly mean, the standard uncertainty of the difference is plotted as infinity. X-axis label is lotus time in days.

The comparison has the following *novel characteristics*: 1) Only flasks with the flags “...” or “..P” are accepted. Also, both members of the pair must be present. *Each pair is substituted by the mean (fm) and the standard deviation (sdf) of the 2 flasks that compose the pair*; 2) Each pair is compared with *the hourly mean (hm) simultaneous in time* (the hourly mean time interval must contain the time of the pair sampling). The standard deviation (sdh) of the sample of

measurements used to compute the hourly mean is also taken into account; 3) *The difference fm-hm and its “internal” standard uncertainty, $\text{SQRT}(\text{sdh}*\text{sdh}+\text{sdf}*\text{sdf})$, are computed for every member of the comparison set. Their time series for each trace gas are showed in Figure 4, where the x-axis is lotus time. Note that when there is only one available injection for the hourly mean, the standard uncertainty of the difference is plotted as infinity. 4) For each trace gas, global and annual mean differences and standard deviations are computed. Three types of means (and standard deviations) are computed: Mean, WMean, and FWMean (as denoted in Figure 5). Mean is the conventional mean. FWMean is a “full” weighted mean computed using the minimum variance method (maximum likelihood for Gaussian distributions). WMean is an “intermediate” weighted mean. A complete description of this method is given by Gomez-Pelaez et al. (2012) and its associated per-review paper. The basic idea is: differences with a larger uncertainty provide information of a lower quality to compute de mean.*

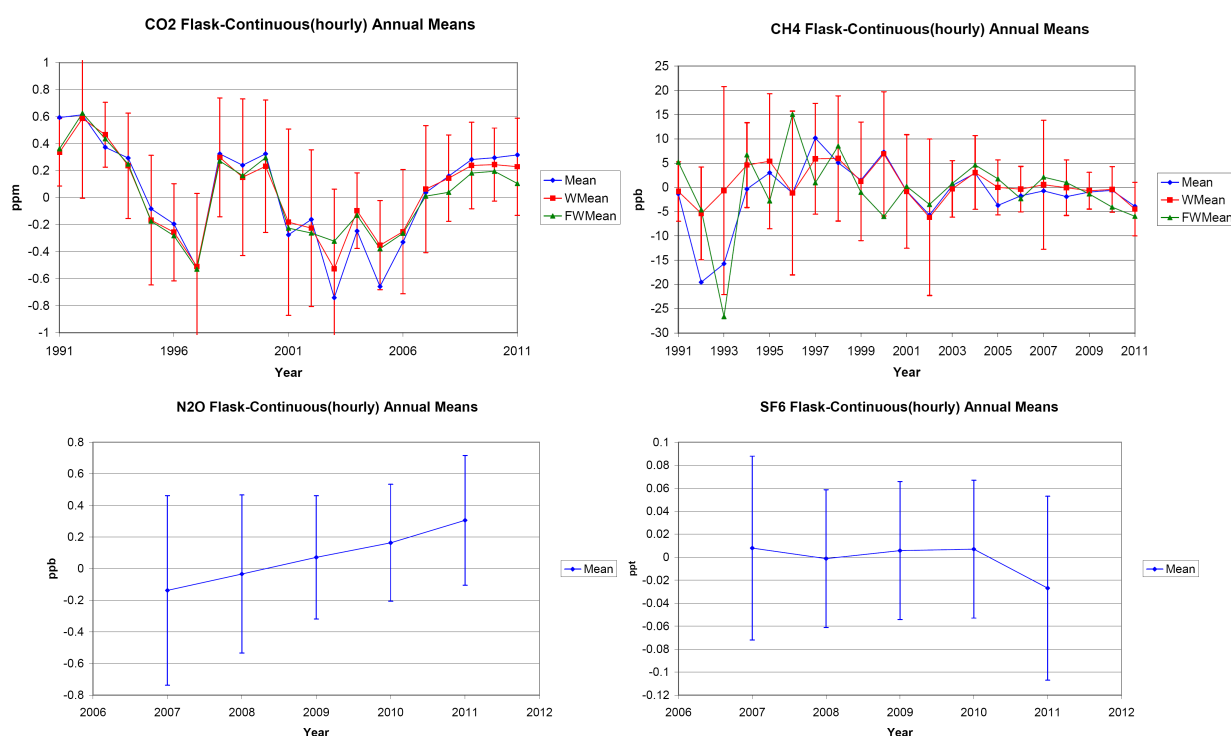


Figure 5. Flask minus continuous mean differences (Mean, WMean, and FWMean) for CO₂, CH₄, N₂O, and SF₆, and associated standard deviation.

Annual means are plotted in Figure 5. *Global means and their standard deviations* are detailed in Table 1. Figure 6 shows the difference distributions for each trace gas.

	Mean	St. dev.	WMean	St. dev.	FWMean	St. dev.
CO₂ (ppm)	0.05	0.66	0.07	0.52	0.09	0.49
CH₄ (ppb)	-1.1	17.7	0.9	11.4	-0.8	7.1
N₂O (ppb)	0.07	0.47				
SF₆ (ppt)	0.0002	0.07				

Table 1. Global mean differences and their standard deviations.

3. Novelties in the CH₄ program, and time series update

See Gomez-Pelaez & Ramos (2011) and references therein for a description of this measurement program. On March 2009, Izaña’s CH₄ program passed satisfactorily a WCC-EMPA scientific audit; see Zellweger et al. (2009).

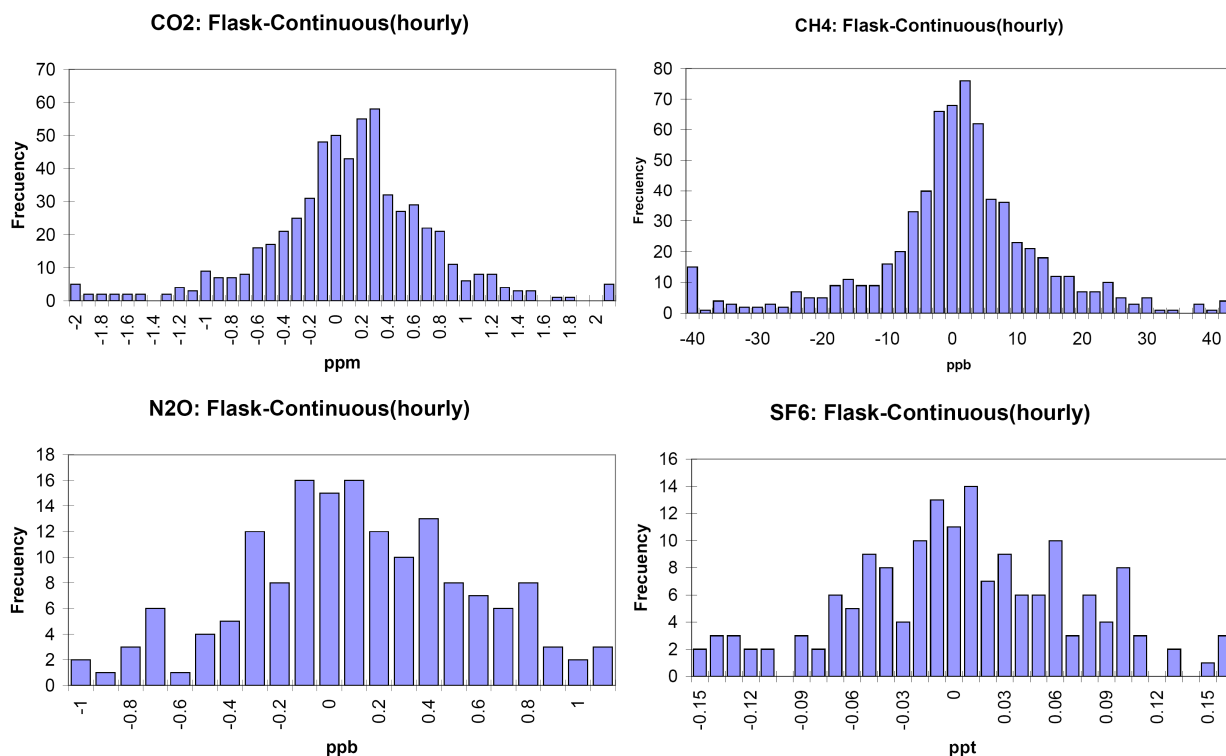


Figure 6. Flask minus continuous difference distributions for CO₂, CH₄, N₂O, and SF₆.

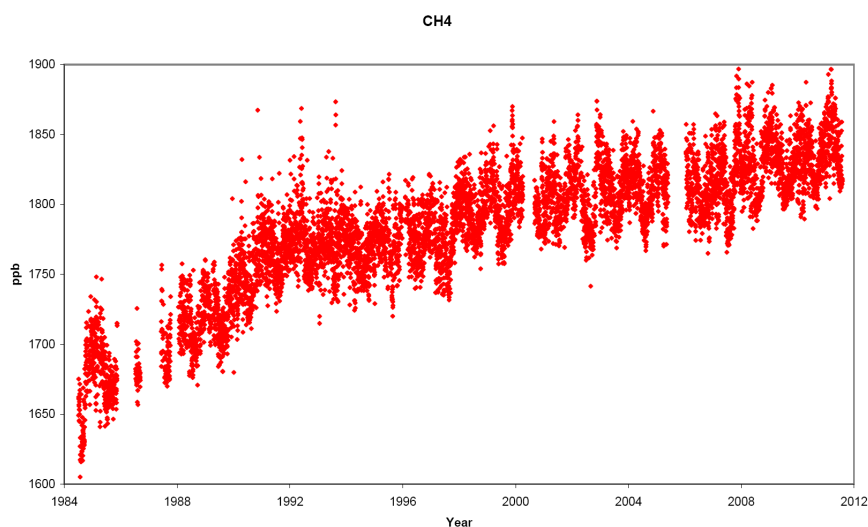


Figure 7. Izaña in-situ measured CH₄ daily night mean (20:00-08:00 UTC).

A *dilution correction* (depending on bath temperature), due to the presence of a very small amount of remaining water vapour in the sample after cryocooling, has been implemented in CH₄ and N₂O data (re)processing for measurements carried out after June 14, 2007. See Gomez-Pelaez & Ramos (2009) for a conceptual description of this correction. As examples, for a CH₄ mole fraction of 1850 ppm, the correction amounts to 0.82 ppb and 0.17 ppb for cryocool bath temperatures of -31°C and -45°C, respectively. Bath temperature usually has been -70°C or smaller since April 2009, being the dilution correction negligible most of the time since then.

For the period April 26, 2006 (lotus time in days: $lt_0=38,833.64$) till May 28, 2008 (lotus time in days: $lt_t=39,596.42$), a significant systematic deviation has been appreciated when comparing continuous in-situ CH₄ data with collocated NOAA flasks (weekly sampling). The reasons of such deviation are still not known. For such period, we have added a cubic (in time)

correction to the continuous in-situ data, being the correction in ppb: $-2.556 \times 10^{-7} \times t^3 + 4.042 \times 10^{-4} \times t^2 - 0.1477 \times t - 14.08$, where $t = It - It_0$, and It is lotus time in days.

4. CO₂ time series update

Gomez-Pelaez et al (2011) describe in detail the in-situ CO₂ measurement system and data processing. Figure 8 shows the update of the Izaña in-situ CO₂ time series.

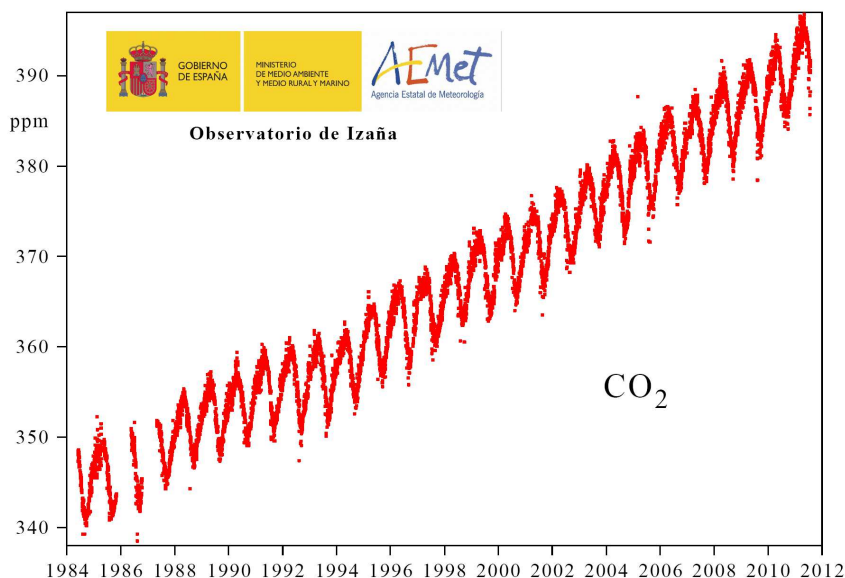


Figure 8. Izaña in-situ measured CO₂ daily night mean (20:00-08:00 UTC).

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