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 N_2O and SF_6, 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 N_2O and SF_6 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 summarizes the results of such comparisons for CO_2, CH_4, N_2O and SF_6. Third, some novelties concerning the in-situ Izaña CH_4 measurements are detailed. Finally, updates of the in-situ CO_2 and CH_4 Izaña time series are showed.

N_2O and SF_6 calibration and ambient data processing

Izaña's N_2O measurement program passed satisfactorily a scientific audit carried out by WCC-N_2O in November 2008; see Scheel (2009). Gomez-Pelaez & Ramos (2009) describes the system to measure N_2O and SF_6 at Izaña station (GC-ECD system configuration, time sequences, and chromatograms), but there have been some changes:

- We have changed the method for locating peak baselines, considering SF_6 as a tangent peak far on the tail of the N_2O peak (instead of forcing a valley baseline), and have reintegrated the full series of chromatograms.
- 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), ambient air (minute 07:30).
- 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.

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 assumed that h/h_{wt} is a quadratic polynomial in N_2O mole fraction, and a linear polynomial in SF_6 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:

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

  where $slope = a_1 + 2a_2 r_{wt}$, 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. Figures 1 and 2 show 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).
- 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).
- For ambient measurements, 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, and finally for the ambient air mole fraction series.
- Dilution correction is applied for N_2O (see below, the second paragraph of the section "Novelties in the CH_4 program" of this presentation).
- A correction, due to a small bias in the ambient air inlet line, is applied to N_2O 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.

Graphics A (in the array of figures) show updated daily night means (20:00-08:00 UTC) of Izaña in-situ CO_2, CH_4, N_2O, and SF_6 atmospheric measurements.

Figure 1

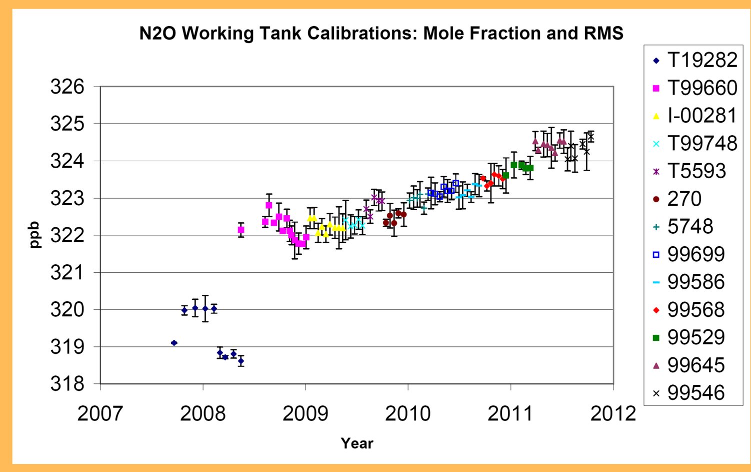
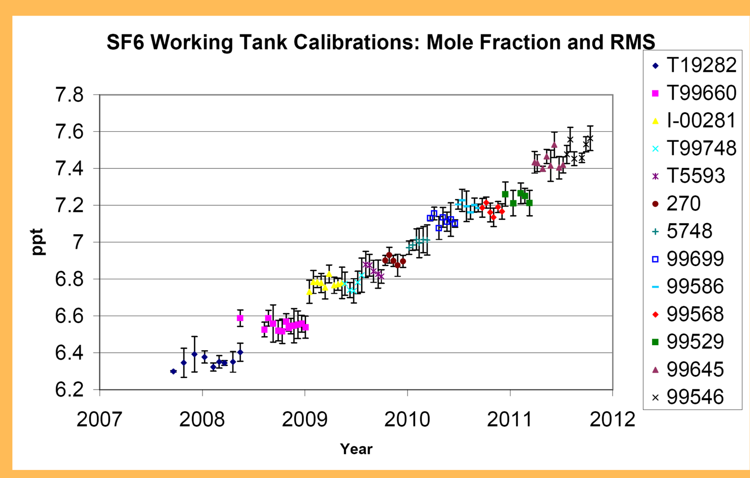


Figure 2



Novelties in the CH_4 program

See Gomez-Pelaez & Ramos (2011) and references therein for a description of this measurement program. On March 2009, Izaña's CH_4 program passed satisfactorily a WCC-EMPA scientific audit; see Zellweger et al. (2009).

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 CH_4 and N_2O 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 CH_4 mole fraction of 1850 ppm, the correction amounts to 0.82 ppb and 0.17 ppb for cryocool bath temperatures of -31ºC and -45ºC, respectively. Bath temperature usually has been -70ºC 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_f=39,596.42), a significant systematic deviation has been appreciated when comparing continuous in-situ CH_4 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 $t = lt - lt_0$, and lt is lotus time in days.

Comparison between flask and continuous measurements

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). The comparison has the following **novel characteristics**:

- 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.
- 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.
- The difference *fm-hm* and its **"internal" standard uncertainty**, *SQRT(sdh*sdh+sdf*sdf)*, are computed for every member of the comparison set. Their time series for each trace gas are showed in graphics B (in the array of figures), where the *x*-axis is lotus time.
- For each trace gas, global and annual difference means and standard deviations are computed. 3 types of means (and standard deviations) are computed: *Mean*, *WMean*, and *FWMean* (as denoted in graphics D). ***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.

Annual means are plotted in graphics D. Global means and their standard deviations have the following values:

	Mean	St. dev.	WMean	St. dev.	FWMean	St. dev.
CO_2 (ppm)	0.05	0.66	0.07	0.52	0.09	0.49
CH_4 (ppb)	-1.1	17.7	0.9	11.4	-0.8	7.1
N_2O (ppb)	0.07	0.47				
SF_6 (ppt)	0.0002	0.07				

References

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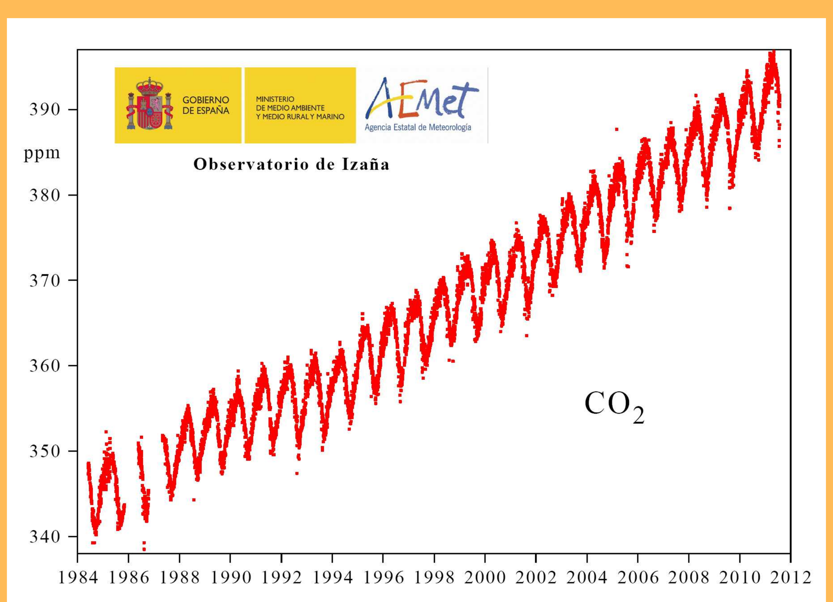
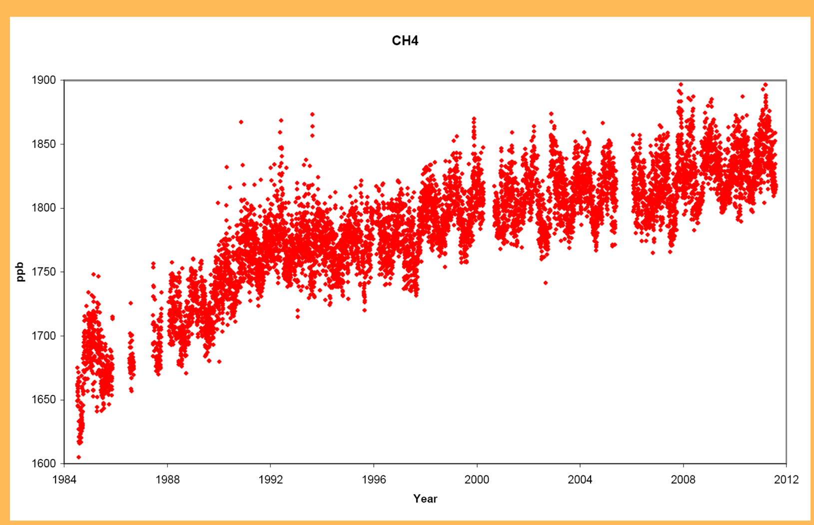
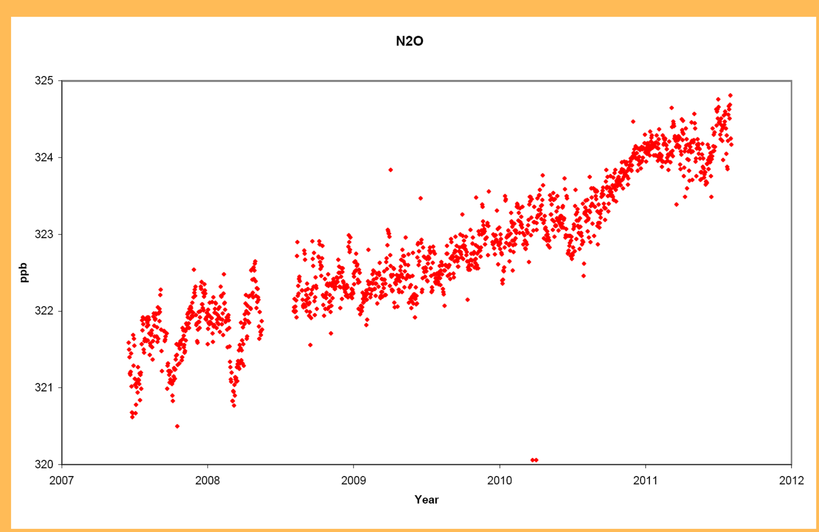
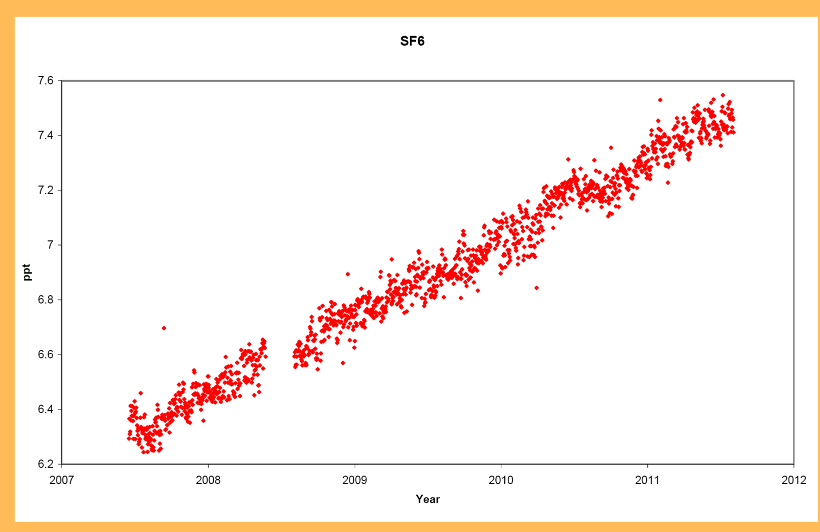
CO_2	CH_4	N_2O	SF_6

A









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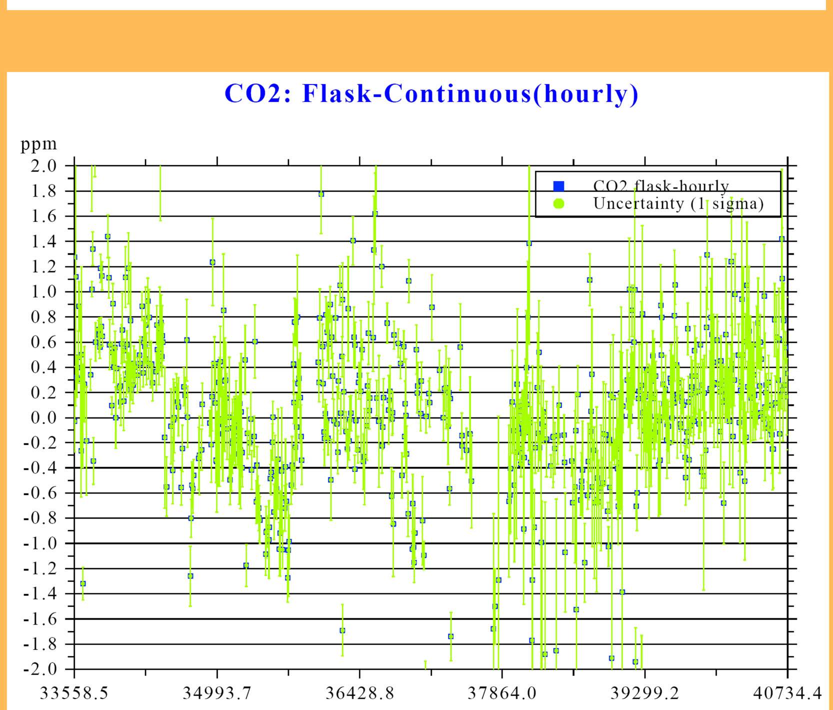

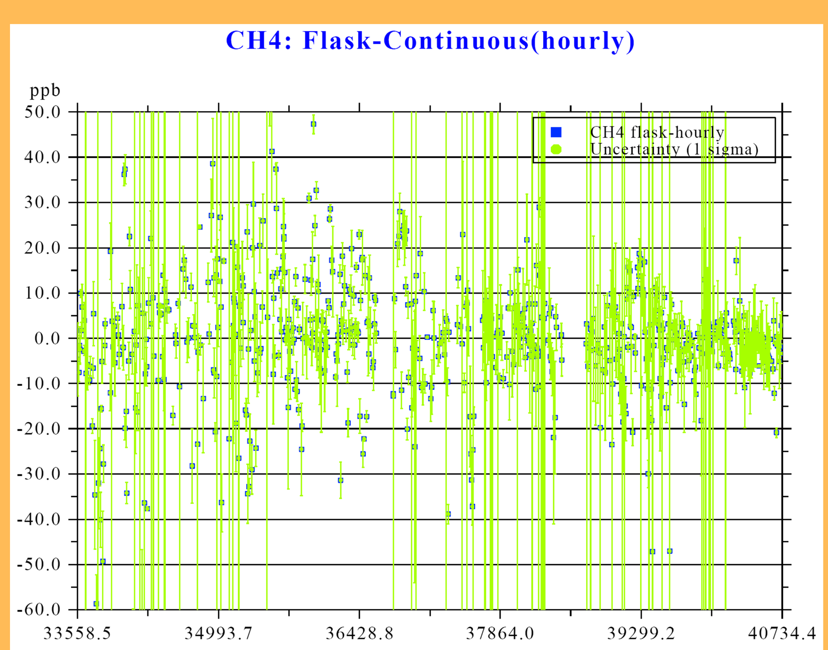

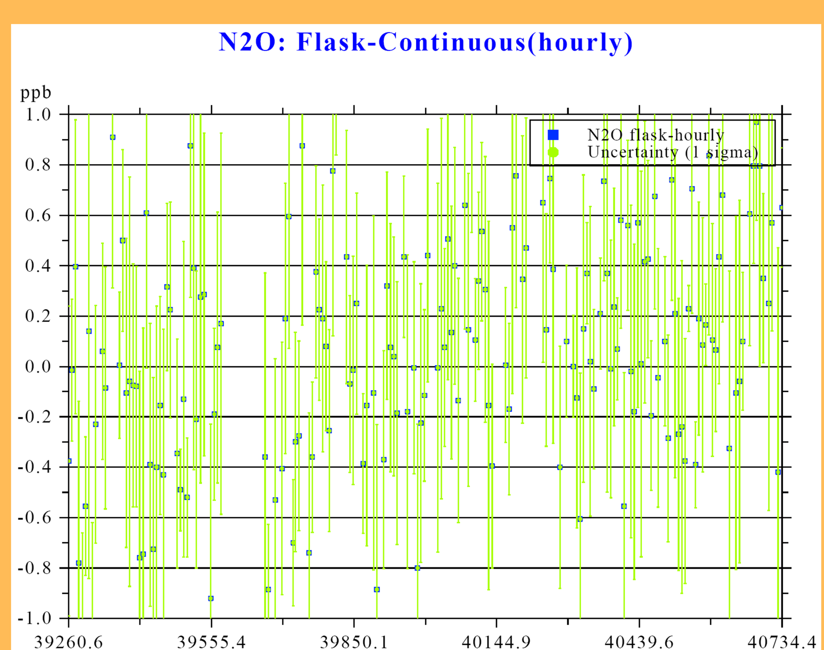

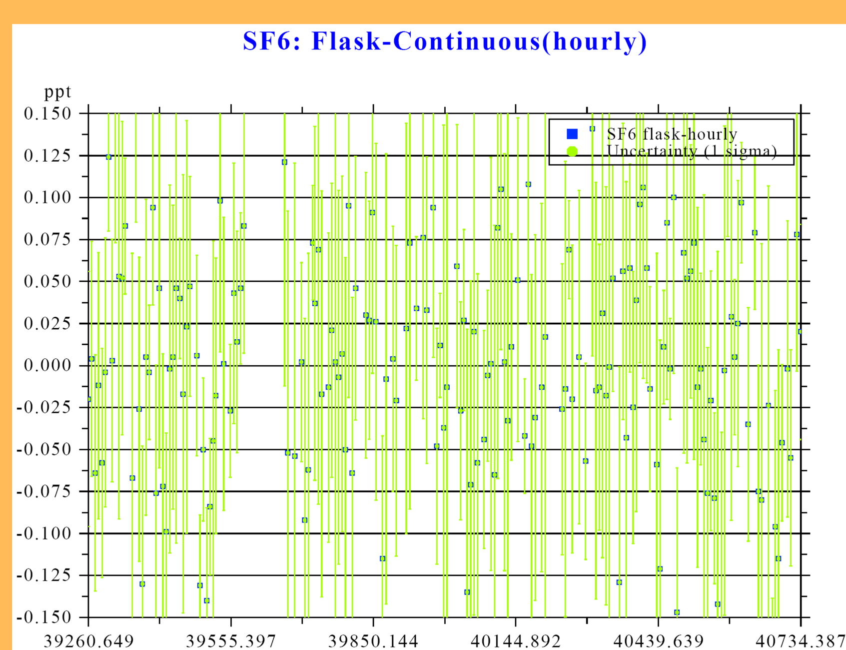

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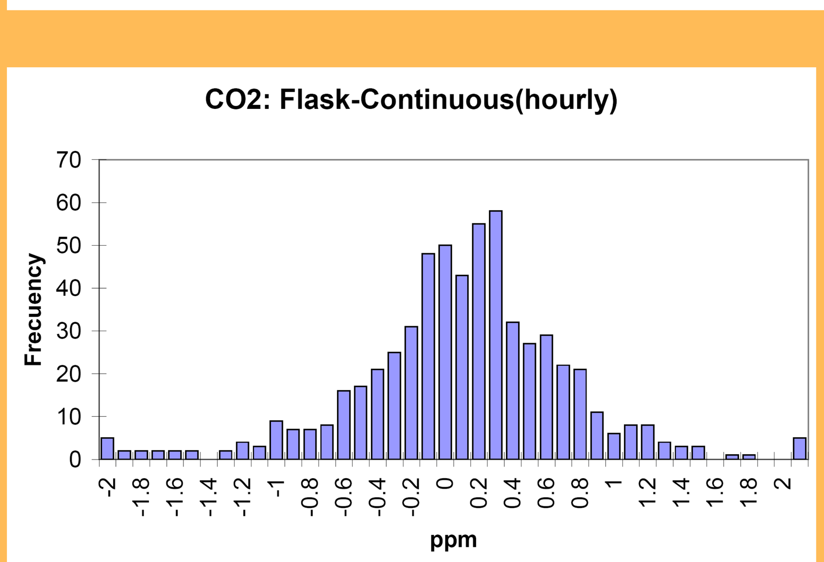

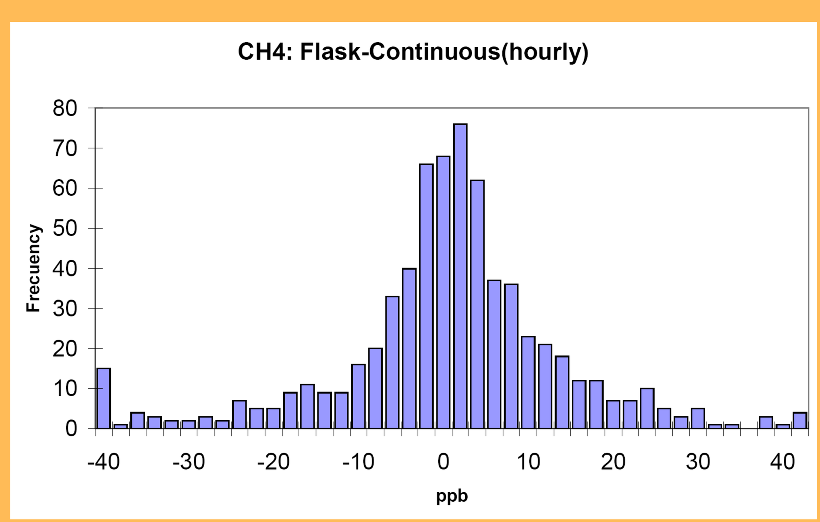

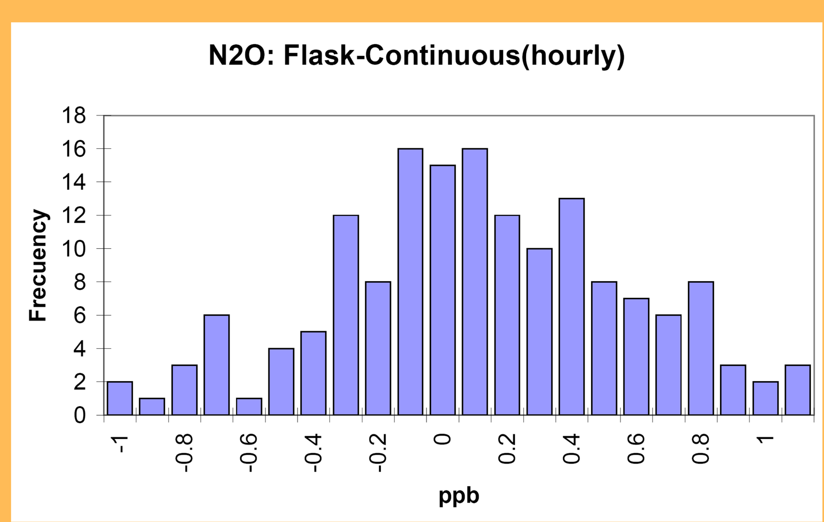

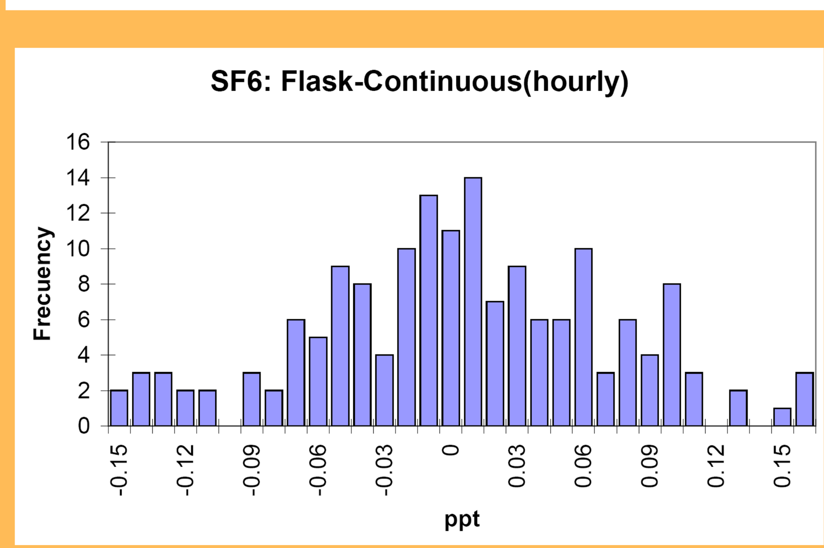

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