# Izaña global GAW station greenhouse-gas measurement programme. Novelties and developments during October 2011 – May 2013

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17th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Tracer Measurement Techniques (Beijing, China, June 10-14, 2013)

## Scheme of the talk:

- Izaña station and its in situ GHG measurement programme
- Publication of an AMT paper about the computation of the uncertainty in measurement
- Mention the Izaña FTIR group's paper about two methods to retrieve tropospheric $CH_4$ mole fraction and the use of the in situ measurements to validate them.
- Installation at Izaña of a system to measure flasks
- Changes introduced in the GHG measurement systems and the data processing software

# Izaña Atmospheric Observatory (IZO) is:

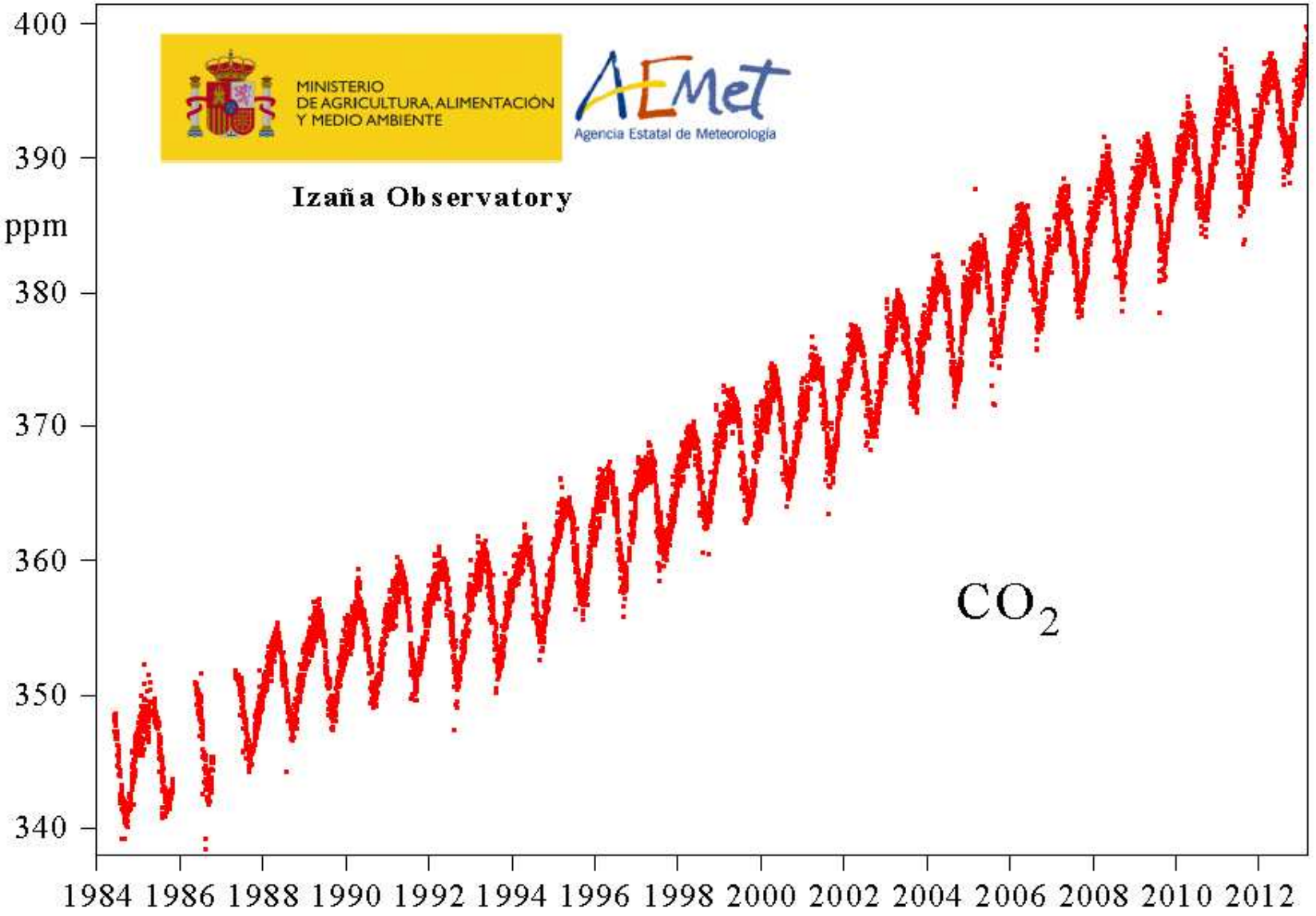
- A Global GAW Station (many measurement programmes additionally to that for in situ GHGs)
- A NDACC Station
- A TCCON Station
- A BSRN Station (radiation)
- An AERONET/PHOTONS Calibration Center and station (aerosols)
- The GAW Regional Brewer Calibration Center for Europe

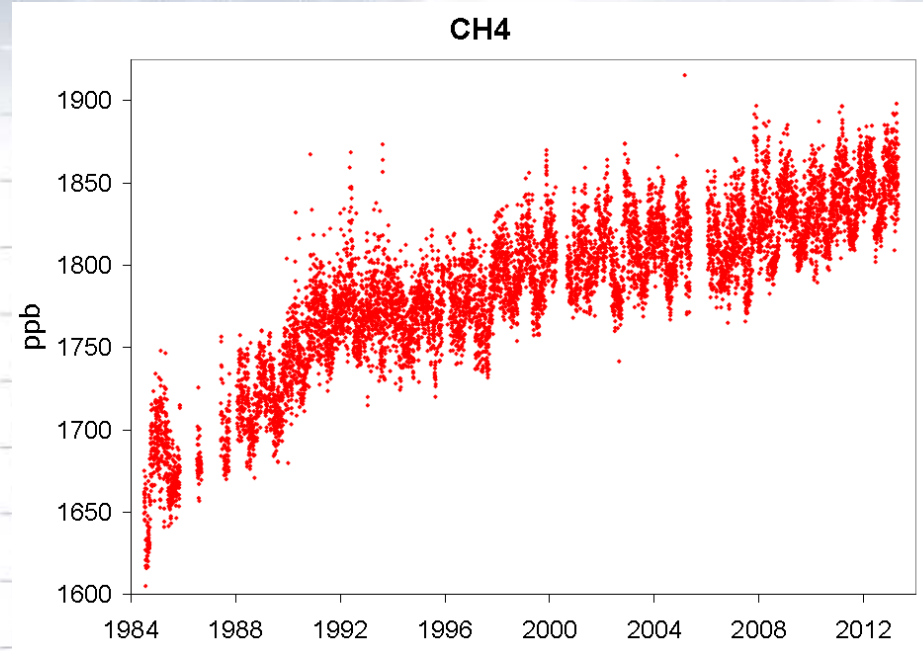


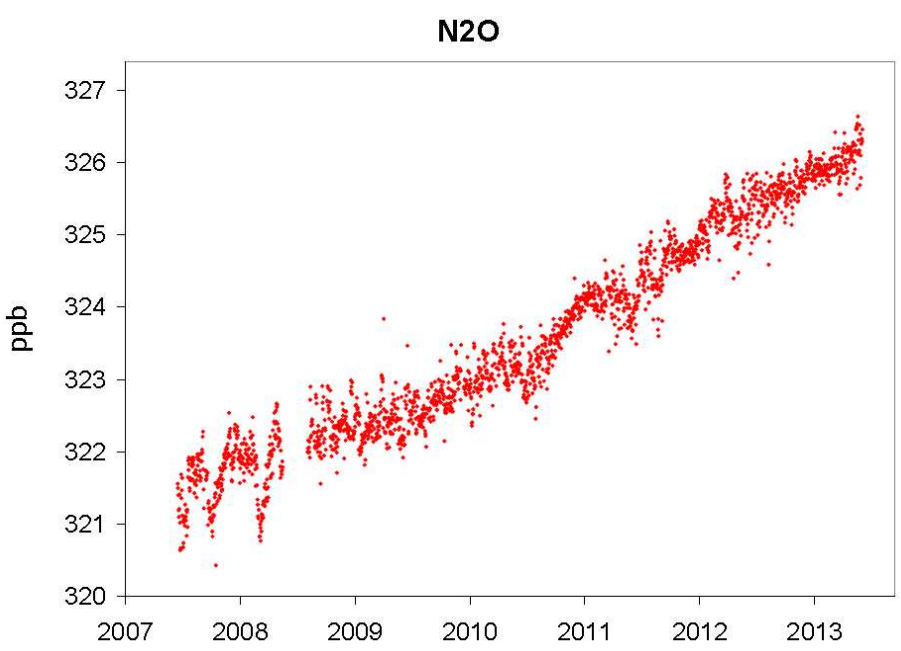
izana.aemet.es

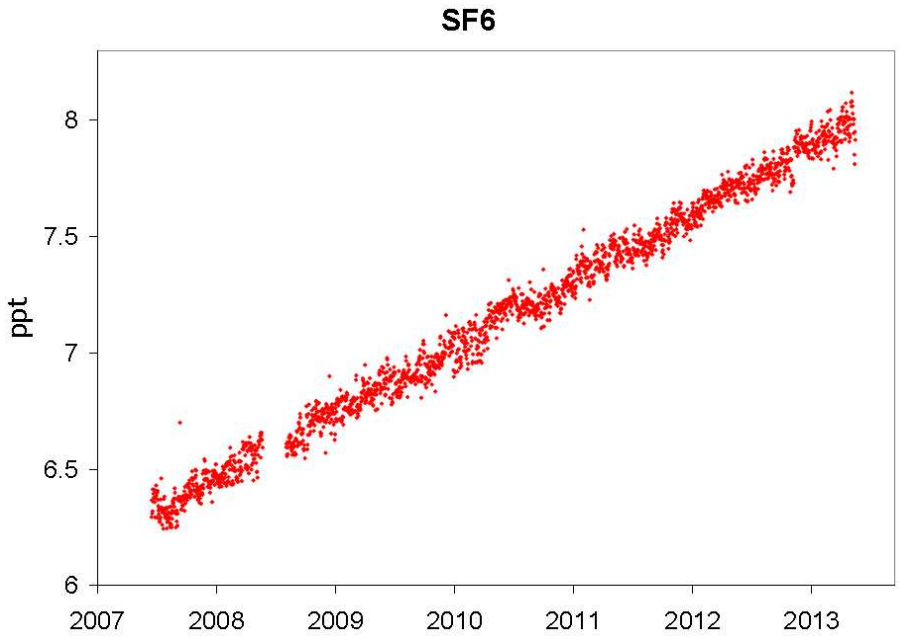
# Gases measured at Izaña using in situ analysers within the greenhouse-gas programme

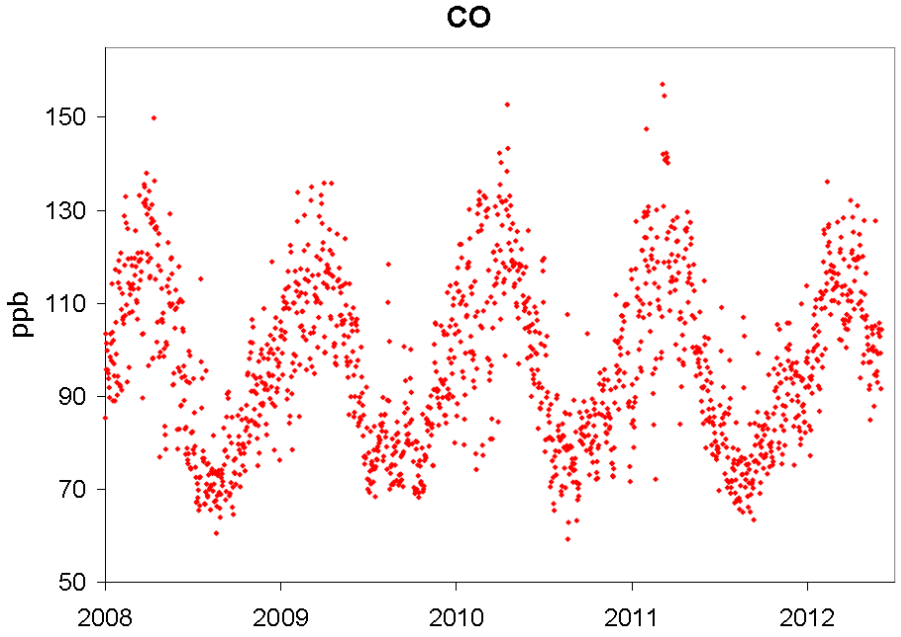
| GAS | Since year | Scale | Analyser | Model |
|---|---|---|---|---|
| **$CO_2$** | 1984 | 1984-1994: WMO-X87<br>1995-2006: WMO-X93<br>2007-present: WMO-X2005 | NDIR | Siemens Ultramat 3: (1984-2006)<br>Licor 7000 (2007-present)<br>Licor 6252 (2008-present) |
| **$CH_4$** | 1984 | WMO-2004 | GC-FID | Dani 3800 (1984-present)<br>Varian 3800 (2011-present) |
| **$N_2O$** | 2007 | WMO-2006 | GC-ECD | Varian 3800 (2007-present) |
| **$SF_6$** | | WMO-2006 | | |
| **CO** | 2008 | WMO-2004 | GC-RGD | Trace Analytical RGA3 |


MINISTERIO DE AGRICULTURA, ALIMENTACIÓN Y MEDIO AMBIENTE
AEMet
Agencia Estatal de Meteorología
Izaña Observatory
ppm
400
390
380
370
360
350
340
CO2
1984 1986 1988 1990 1992 1994 1996 1998 2000 2002 2004 2006 2008 2010 2012


CH4
ppb
1900
1850
1800
1750
1700
1650
1600
1984
1988
1992
1996
2000
2004
2008
2012


N2O
ppb
327
326
325
324
323
322
321
320
2007
2008
2009
2010
2011
2012
2013


SF6
ppt
8
7.5
7
6.5
6
2007
2008
2009
2010
2011
2012
2013


CO
ppb
150
130
110
90
70
50
2008
2009
2010
2011
2012

**Cooperations.** We collect:

- Flask samples for NOAA-ESRL-GMD-CCGG since 1991
- 2-week integrated samples of $^{14}CO_2$ for the University of Heidelberg since 1984

**Recent comparison exercices:**

- Flask versus in-situ continuous measurements
- Participation in the 5$^{th}$ WMO Round Robin
- Audits by WCC-N2O (2008) and WCC-CH4-CO (2009)

## We are trying to install also an ICOS station at the Izaña observatory

Pursuing this objective, AJGP attended the two Atmospheric ICOS Workshops that held during 2012, and participated in one of the working groups designated in the first of these workshops (WG 6: Quality management for atmospheric ICOS stations).

However, we have not obtained funds to buy the required instrumentation and to pay to ICOS the required annual station fee. Now is clear, that there is no possibility of getting such funds during the next few years. So, most likely, we are not going to install any atmospheric ICOS station at Izaña during the next 4 or 5 years.

# Computation of uncertainty

In cooperation with Paul Novelli (NOAA), we have published the following paper in the GGMT-2011 special issue of AMT:

Gomez-Pelaez, A. J., Ramos, R., Gomez-Trueba, V., Novelli, P. C., and Campo-Hernandez, R.: A statistical approach to quantify uncertainty in carbon monoxide measurements at the Izaña global GAW station: 2008-2011, Atmos. Meas. Tech., 6, 787-799, doi:10.5194/amt-6-787-2013, 2013

**This paper presents mainly a method to rigourously quantify the uncertainty in the CO measurements carried out at the Izaña station using a GC-RGD (RGA). This method could be applied to other GAW stations, not only for CO but also for other GHG measurements (specially if they are carried out using a GC).**

We compute the combined standard uncertainty as a quadratic combination of four uncertainty components:

1) the uncertainty of the laboratory standards interpolated over the range of measurement,
2) the uncertainty that takes into account the agreement between the standard gases and the response function used,
3) the uncertainty due to the repeatibility of the injections, and
4) the propagated uncertainty related to the temporal consistency of the response function parameters.

The paper provided mathematical expressions for all these components.

Additionally, the paper points out how to compute the uncertainty of temporal means: each uncertainty component has to be propagated in a way that depends on its random or systematic character, and then all components have to be added quadratically.

# Paper comparing FTIR and in-situ measurements

KIT-IMK has a FTIR at Izaña Observatory since 1999. This spectrometer is operated in cooperation with IARC.

This FTIR is a member of the NDACC and TCCON networks, and measures column density and vertical profile for many trace gases, and in particular, many GHGs.

**KIT-IMK FTIR group**

T. Blumenstock

F. Hase

M. Schneider

S. Dohe

**IARC FTIR group**

O.E. García

E. Sepúlveda

I would like to bring to your attention the following paper prepared by the IARC and KIT-IMK FTIR groups in cooperation with the IARC in situ GHG group.

Sepúlveda, E., M. Schneider, F. Hase, O. E. García, A. Gomez-Pelaez, S. Dohe, T. Blumenstock, and J.C. Guerra, Long-term validation of tropospheric column-averaged CH4 mole fractions obtained by mid-infrared ground-based FTIR spectrometry, Atmos. Meas. Tech., 5, 1425-1441, doi:10.5194/amt-5-1425-2012, 2012

The paper presents two methods to retrieve tropospheric CH4 mole fraction and uses the in situ measurements for the period 2001-2010 to validate them. The FTIR measurements obtained with the best of the two methods have a **compatibility** with the in-situ CH4 measurements characterized by:

Mean difference of the daily means = -0.13 % (~ -2.4 ppb)

Standard deviation of the differences = 0.97 % (~ 17.6 ppb)

# Installation of a system to measure flasks at Izaña

- We have almost finished **installing at Izaña a system to measure GHG** mole fractions in air samples stored **in flasks.**

- The system is **based on some of the instruments used at Izaña to carry out continuous GHG measurements.**

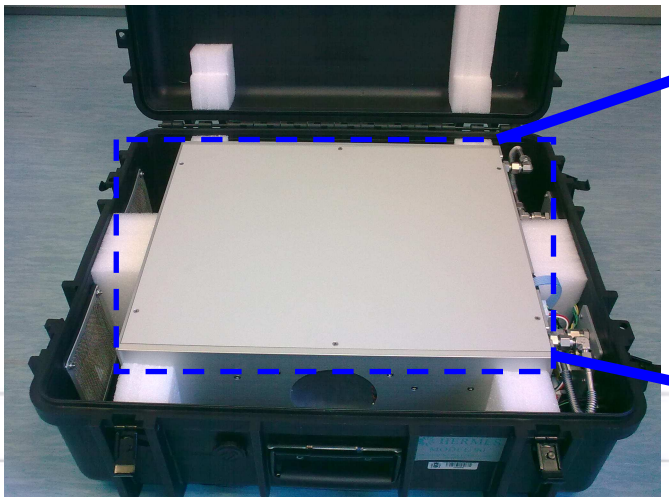
- This means there will not be in situ measurements by these instruments while flasks are being measured. This is not a problem since **flask measurements are going to be occasional and only during daytime** (background conditions hold at Izaña during night-time).

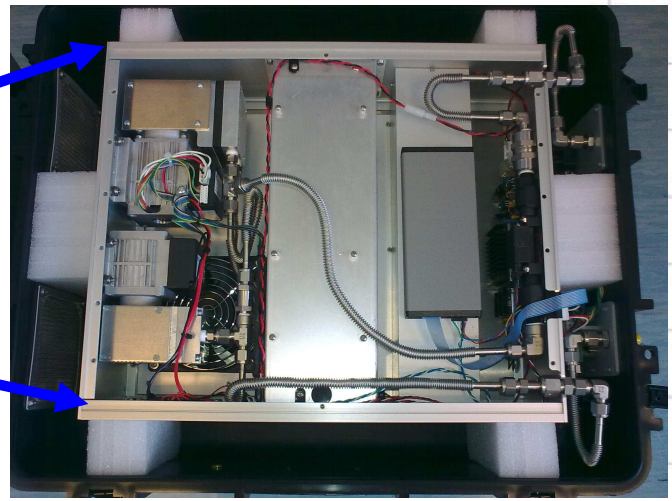
- Air samples will be collected mainly **on board an aircraft flying near Izaña** to get in situ atmospheric **vertical profiles** of trace gases in the framework of occasional campaigns promoted by financed projects; **e.g. MUSICA** (http://www.imk-asf.kit.edu/english/musica.php ; MUlti-platform remote Sensing of Isotopologues for investigating the Cycle of Atmospheric water) in July 2013.


- Additionally to the intrinsic value of the in situ vertical profiles, we will **compare** them **with column measurements carried out by the Izaña FTIR and by the IASI instrument** (on board a satellite).

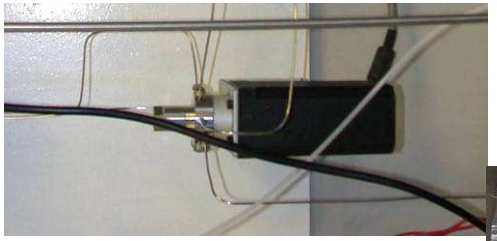
- The flasks to be measured are contained in two PFPs (Programmable Flask Packages).
- Air sampling will be carried out using a PFP connected in series with a PCP (Programmable Compressor Package).

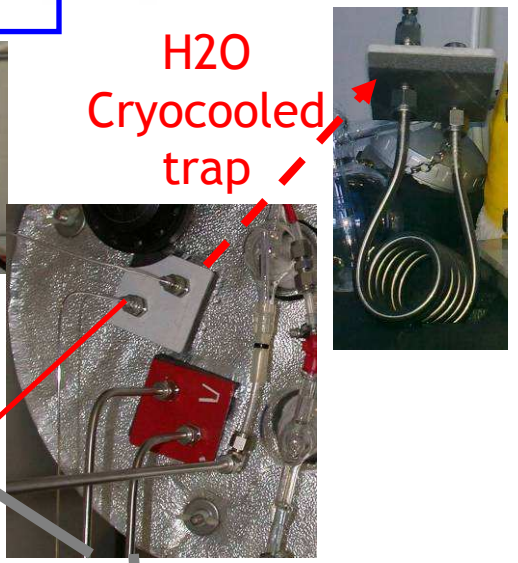
PFPs and PCP purchased by AEMET at the end of 2011. **They were designed by NOAA-ESRL-GMD-CCGG** and manufactured by HPD.

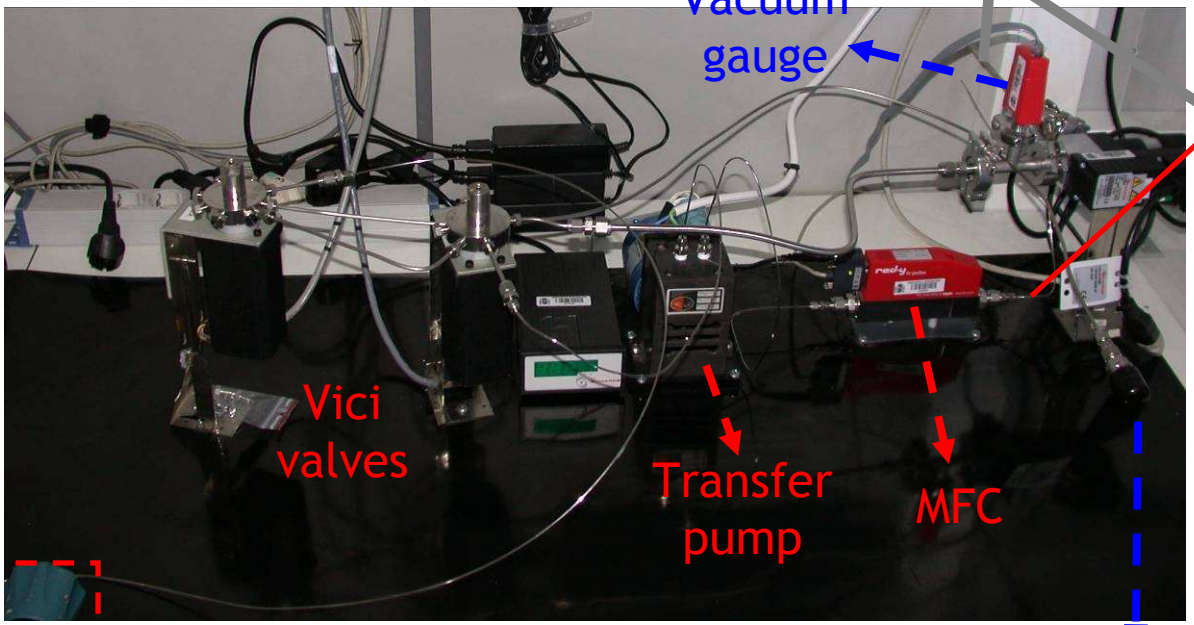




The system we have implemented to vacuum the PFP manifold, extract air from the flasks and distritute it to the instruments is similar to MAGIC (NOAA-ESRL-GMD-CCGG). The control software has been created at Izaña.

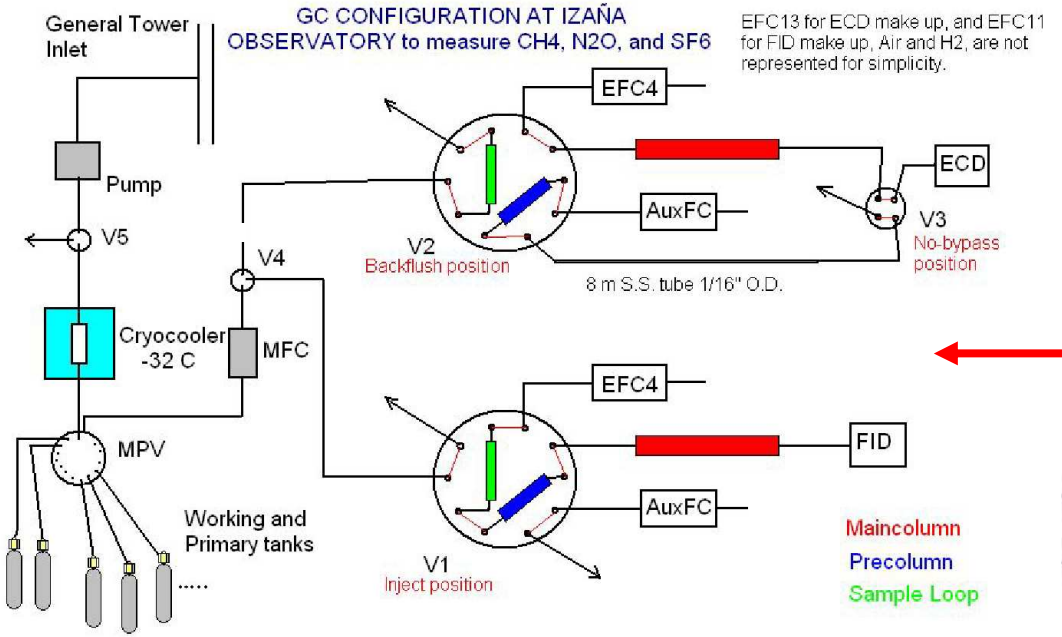



# Changes introduced in the GHG measurement systems

In our old GC-FID (Dani), the sample loop always had been out of the column oven. In May 2012 we introduced it inside the oven. In June 2012, we installed a new FID temperature controller, and selected a new FID temperature: 225ºC instead of 110ºC.

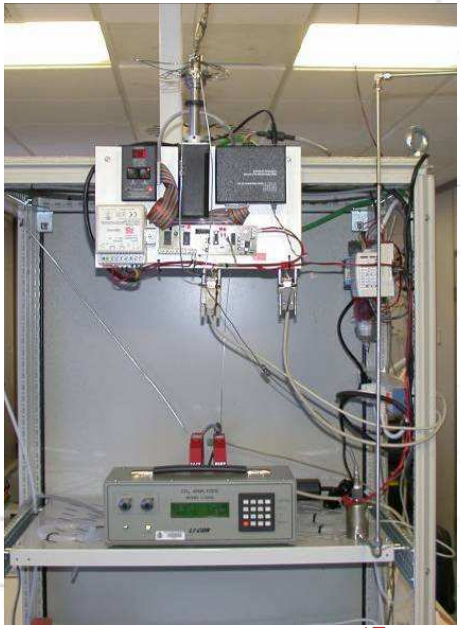



In August 2012, we changed slighly the temporal programming of the 3-port-2-position solenoidal valve V4 of the GC-Varian, because we realise that when a GC injection valve is in inject position, the sample loop contains carrier gas at a pressure significantly higher than ambient. So, when the valve goes to load position, the carrier gas inside the loop will expand and partly go out of the loop. If in that moment the inlet of the loop is not closed, perhaps a small amount of carrier gas might reach MFC (and finally reach the other sample loop; and it seems undesirable, specially the possibility that some Ar/CH4 of the ECD system might reach the loop of the FID system, in spite of the fact that such loop is going to be flushed)

## Before

Before April 1, 2013 we had the two NDIR of Izaña working in series. After this date, they were separated completely, and since then, each one has its own laboratory standards, working stantadards and ambient inlet line.

## After



# Changes introduced in the raw data processing software

- We submit to the WDCGG hourly, daily and monthly means. The daily and monthly means we was submitting included the 24 hours of every day. In August 2011, we recomputed for all the time series, the daily and monthly means using only data from 20:00 to 08:00 UTC (nighttime pure background conditions), and resubmitted them to the WDCGG.

- For the data processing of the CO2 measured with the Licor-7000, we apply a F-Snedecor test to decide if a working standard is drifting in time. We required a 99% confidence level to reject the hypothesis of no drifting. In May 2012, we decided to use a 95% confidence level, and then reprocesed and resubmitted the whole time series measured with this instrument.

- Licor-7000: we measure three working gases from minute 30:00 to 39:00 of every hour, whereas the rest of the hour we measure ambient air. But the first minute after 39:00 is discarded. In May 2012, we implemented the rejection of four minutes instead of one for the period 2007-August 2010, due to a flow transition problem we identified and solved in September 2010. Then, we reprocessed and resubmitted the time series.

AJGP is grateful to Doug Guenther, Anna Karion and Jack Higgs for providing information about the PFPs and PCPs; and to Andrew Crotwell and Tom Conway for providing information about MAGIC (NOAA-ESRL-GMD-CCGG).

## Thank you for your attention !