

IZAÑA GLOBAL GAW STATION GREENHOUSE-GAS MEASUREMENT PROGRAMME. NOVELTIES AND DEVELOPMENTS DURING OCTOBER 2011 – MAY 2013

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1. The Izaña Atmospheric Observatory

The Izaña Atmospheric Observatory (IZO) is run by Izaña Atmospheric Research Center (IARC), which belongs to the Meteorological State Agency of Spain (AEMET). IZO is located on the top of a mountain (28.309° N, 16.499° W, 2373 m a.s.l.) on the island of Tenerife (Canary Islands, Spain), well above a strong subtropical temperature inversion layer. In situ measurements at Izaña are representative of the subtropical Northeast Atlantic free troposphere, especially during the night period. The Izaña Atmospheric Observatory is: a Global GAW station (with many measurement programmes additionally to that for in situ greenhouse gases), a NDACC station, a TCCON station, a BSRN station (radiation), an AERONET/PHOTONS calibration centre and station (aerosols), the GAW Regional Brewer Calibration Centre for Europe... More information about IZO can be obtained visiting its web site: izana.aemet.es



Figure 1 – The Izaña Atmospheric Observatory from two different viewpoints.

IARC would like to install also an ICOS (Integrated Carbon Observation System) 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.

2. In situ greenhouse-gas measurements at the Izaña observatory

IARC (AEMET) measures using in situ analysers at Izaña several atmospheric gases within the greenhouse-gas programme as Table 1 details. Figures 2 and 3 show the time series of daily nighttime (20:00 – 08:00 UTC) mean mole fractions measured at Izaña for each gas. See Gomez-Pelaez et al. (2012) and references there in, and Gomez-Pelaez et al. (2013) for details about the measurement systems (these references also are available at the IARC web site izana.aemet.es).

GAS	Since year	Scale	Analyser	Model
CO ₂	1984	1984-1994: WMO-X87 1995-2006: WMO-X93 2007-present: WMO-X2005	NDIR	Siemens Ultramat 3: (1984-2006) Licor 7000 (2007-present) Licor 6252 (2008-present)

CH₄	1984	WMO-2004	GC-FID	Dani 3800 (1984-present) Varian 3800 (2011-present)
N₂O	2007	WMO-2006	GC-ECD	Varian 3800
SF₆		WMO-2006		
CO	2008	WMO-2004	GC-RGD	Trace Analytical RGA3

Table 1 – Gases measured at Izaña using in situ analysers within the greenhouse-gas programme. The table indicates for each gas: the year in which the measurements started, and the scale and analyser used.

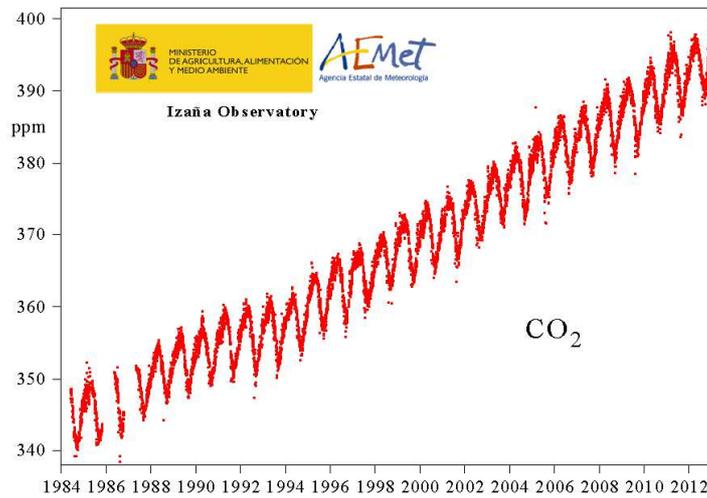


Figure 2 – Daily nighttime (20:00 – 08:00 UTC) mean CO₂ mole fractions measured at IZO.

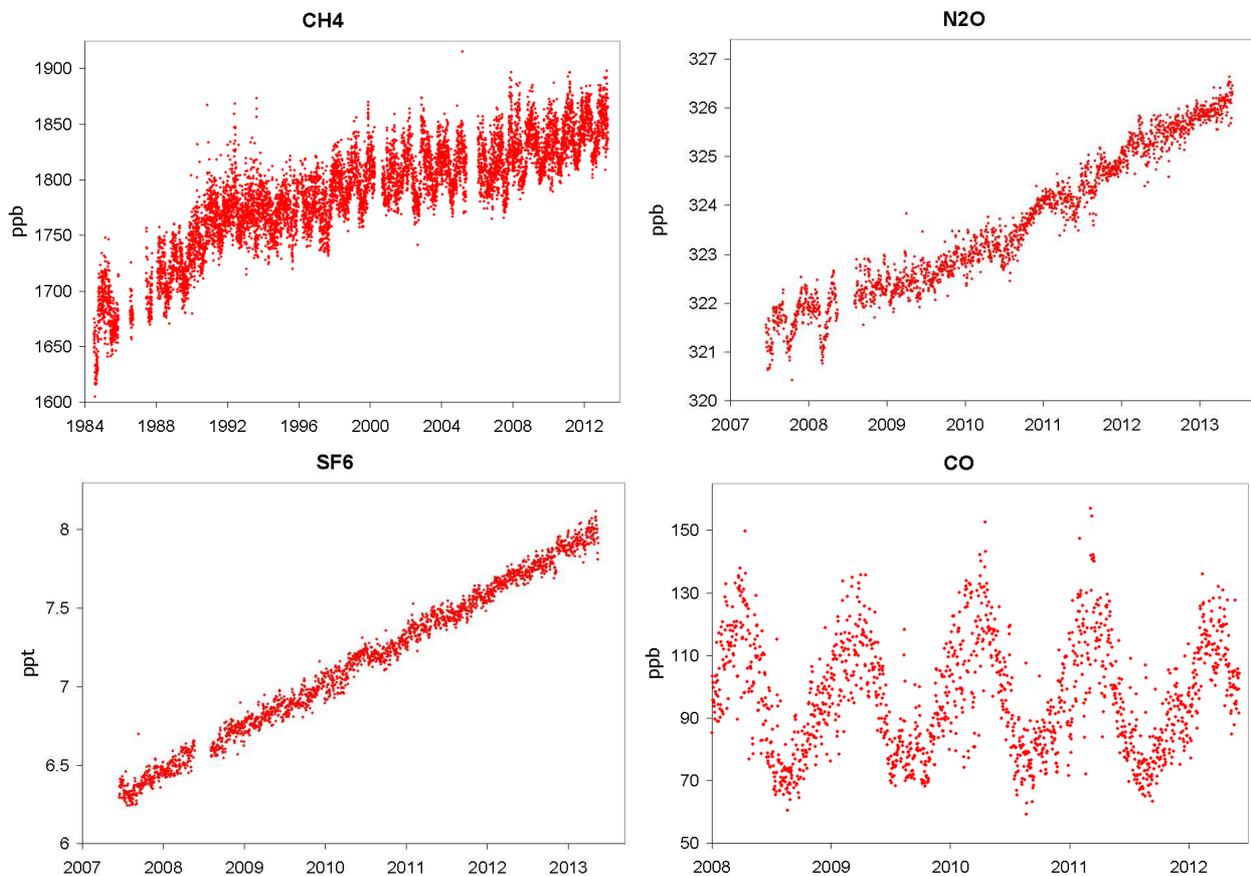


Figure 3 – Daily nighttime (20:00 – 08:00 UTC) mean CH₄, N₂O, SF₆ and CO mole fractions measured at IZO.

Additionally, as cooperation with other institutions, we have collected weekly flask samples for NOAA-ESRL-GMD-CCGG since 1991, and 2-week integrated samples of $^{14}\text{CO}_2$ for the University of Heidelberg since 1984.

Some recent comparison exercises in which IZO was involved: 1) we perform comparisons between flask (NOAA) and in situ continuous (IARC-AEMET) measurements; 2) IARC participated in the 5th WMO Round Robin; 3) the last GAW GHG audits performed at Izaña were conducted by WCC-N₂O in 2008 and WCC-CH₄-CO in 2009.

3. Changes introduced in the GHG measurement systems

In the IZO old GC-FID (Dani 3800), 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: 225 °C instead of 110 °C.

In August 2012, we changed slightly the temporal programming of the 3-port-2-position solenoidal valve V4 (which has one inlet for the air to be analysed, and two outlets: one connected to the sample loop of the GC-FID and another one connected to the sample loop of the GC-ECD) of the GC-Varian (see Figure 1 of Gomez-Pelaez&Ramos, 2009) to prevent the potential problem detailed as follows. We realised that when a GC injection valve is in inject position, the sample loop contains carrier gas at a pressure significantly higher than the ambient one. Therefore, when the valve goes to load position, the carrier gas inside the loop expands and partly goes out of the loop. If in this moment the inlet of the loop is not closed at valve V4, perhaps a small amount of the carrier gas might reach the mass flow controller located just upstream of valve V4 and then reach the other sample loop. This seems to be undesirable, especially the possibility that some Ar/CH₄ of the GC-ECD system might reach the loop of the GC-FID system, in spite of the fact that such loop is flushed after such hypothetical event.

Before April 1st, 2013, two NDIRs were working in series at Izaña measuring CO₂. After that date, they were separated completely (see Figure 4), and since then, each one has had its own laboratory standards, working standards and ambient inlet line.



Figure 4 – IZO's Licor-7000 (left picture) and Licor-6252 (right picture) after their complete separation in April 2013.

4. Changes introduced in the raw data processing software

IZO submits to the WDCGG hourly, daily and monthly means for all the gases within the greenhouse-gas programme. The daily and monthly means we had been 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. We have continued submitting data in this new way since then.

For the raw data processing of the CO₂ measured at Izaña with the Licor-7000, we apply F-Snedecor tests to decide if the working standards have drifted in time (see Gomez-Pelaez&Ramos, 2011). We had been requiring a 99% confidence level to reject the hypothesis of no drifting. However, in May 2012, we decided to use a 95% confidence level, and then we reprocessed (and resubmitted to the WDCGG) using this criterion the whole time series measured with this instrument.

The IZO Licor-7000 measures three working gases from minute 30:00 till 39:00 of every hour, whereas the rest of the hour this instrument measures ambient air. We had been discarding only the first minute after minute 39:00 (cell flushing). However, in May 2012, we implemented the rejection of four minutes instead of one for the period January 2007-August 2010, due to a flow transition problem that we identified and solved in September 2010. Then, we reprocessed (and resubmitted to the WDCGG) the time series.

5. Published peer-review article concerning CO measurement uncertainty

In cooperation with Paul Novelli (NOAA-ESRL-GMD-CCGG), we have published the peer-review article Gomez-Pelaez et al. (2013) in AMT (GGMT-2011 special issue). This paper presents mainly a method to rigorously 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 (especially if they are carried out using a GC).

We would like to bring to the attention of the reader the paper Sepúlveda et al. (2012), which was prepared by the IARC (O.E. García and E. Sepúlveda) and KIT-IMK FTIR (T. Blumenstock, F. Hase, M. Schneider and S. Dohe) groups in cooperation with the IARC in situ GHG group. This paper uses IZO in situ CH₄ measurements to validate tropospheric column-averaged CH₄ mole fractions obtained by the mid-infrared ground-based FTIR spectrometer which has been in operation at Izaña since 1999.

6. Installation of a system to measure flasks at Izaña

By the end of May 2013, we had 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 IZO to carry out continuous GHG measurements. This means that in situ measurements will not be carried out 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 IZO during nighttime).

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-AMISOC campaign in July 2013). Additionally to the intrinsic value of the in situ vertical profiles, they will be compared 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; see Figure 5). Air sampling will be carried out using a PFP connected in series with a PCP (Programmable Compressor Package). IARC-AEMET purchased at the end of 2011 two PFPs and one PCP. 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 distribute it (see Figure 5) to the instruments is similar to that used in MAGIC (the system that NOAA-ESRL-GMD-CCGG uses to measure flasks). The control software has been created at IARC.

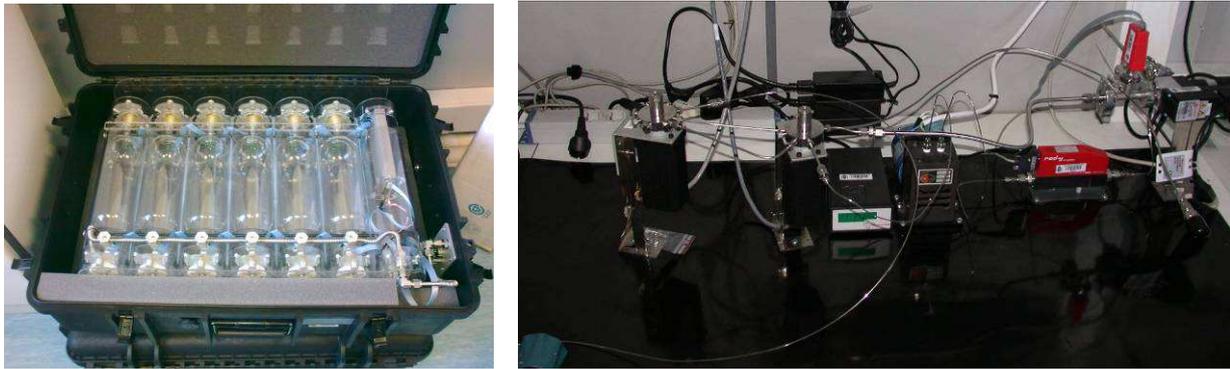


Figure 5 – Left picture: interior of a PFP. Right picture: a part of the system implemented at IZO to vacuum the PFP manifold, extract air from the flasks and distribute it to the instruments.

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References

- Gomez-Pelaez, A.J., Ramos, R., "Installation of a new gas chromatograph at Izaña GAW station (Spain) to measure CH₄, N₂O, and SF₆" in GAW Report (No. 186) of the "14th WMO/IAEA meeting of experts on Carbon dioxide, other greenhouse gases, and related tracers measurement techniques (Helsinki, Finland, 10-13 September 2007)", edited by Tuomas Laurila, World Meteorological Organization (TD No. 1487), Geneva, Switzerland, 55-59, 2009
- Gomez-Pelaez, A.J., Ramos, R., "Improvements in the Carbon Dioxide and Methane Continuous Measurement Programs at Izaña Global GAW Station (Spain) during 2007-2009", in GAW report (No. 194) of the "15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases, and Related Tracer Measurement Techniques (Jena, Germany; September 7-10, 2009)", edited by Willi A. Brand, World Meteorological Organization (TD No. 1553), Geneva, Switzerland, 133-138, 2011
- Gomez-Pelaez, A. J., Ramos, R., Gomez-Trueba, V., Campo-Hernandez, R., Dlugokencky, E., and Conway, T.: "New improvements in the Izaña (Tenerife, Spain) global GAW station in-situ greenhouse gases measurement program", in GAW report (No. 206) of the "16th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (Wellington, New Zealand, October 25-28, 2011)", edited by Gordon Brailsford, World Meteorological Organization, Geneva, Switzerland, 76-81, 2012.
- 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.
- Sepúlveda, E., Schneider, M., Hase, F., García, O. E., Gomez-Pelaez, A., Dohe, S., Blumenstock, T., and Guerra, J. C.: 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.