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GGMT-2015 IZAÑA STATION UPDATE: INSTRUMENTAL AND PROCESSING SOFTWARE DEVELOPMENTS, SCALE UPDATES, AIRCRAFT CAMPAIGN, AND PLUMBING DESIGN FOR CRDS

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1. Introduction

Izaña observatory (IZO) is a GAW Global station located at 2373 m a.s.l. on Tenerife (Canary Islands, Spain). In situ measurements at Izaña are representative of the subtropical Northeast Atlantic free troposphere, especially during the night-time period. **Several atmospheric greenhouse gases (CO2, CH4, N2O and SF6; and the related tracer CO) are measured in situ and continuously at this station**. The recently published **WMO/GAW report N. 219, “Izaña Atmospheric Research Center Activity Report 2012-2014”** (Cuevas et al., 2015), provides detailed information about the different measurement programmes of this supersite. This report is available at the WMO/GAW website: http://www.wmo.int/pages/prog/arep/gaw/documents/Final_GAW_Report_No_219.pdf

In the present GGMT-2015 contribution, **we summarize the more relevant facts and novelties** concerning the IZO GHG in situ measurement programme that have happened **since GGMT-2013**.

Izaña GAW Global station continues **submitting data to the WDCGG** for these 5 GHGs (and related tracer) and participating in the data products **GLOBALVIEW and OBSPACK** led by NOAA-ESRL-GMD-CCGG.

From the end of September 2013 till the beginning of February 2014, **GAW WCC-EMPA conducted a scientific audit at Izaña station** (see Zellweger et al., 2015). That was the first IZO GHG audit in which a travelling instrument has been used (additionally to the usual measurements of travelling standards) to measure ambient air during several months in parallel with the in situ IZO GHG measurements.

Izaña has also participated in the **6th WMO/IAEA Round Robin Comparison Experiment**. We received the two round robin cylinders of Circuit 1 in July 2015, measured them for CO2, CH4, N2O, SF6 and CO, shipped them back to NOAA, and reported the measurement results using the dedicated Round Robin website. The results of this inter-comparison were made public on 9 September 2015 (http://www.esrl.noaa.gov/gmd/ccgg/wmorr/).

2. Instrumental and processing software developments

In October 2013, we installed a **new system of UV lamp** (kindly provided by the Carbon Cycle Group of the Institute of Environmental Physics of the University of Heidelberg) in the **IZO RGA-3**, because spare UV lamps for this old instrument were not being manufactured any longer. This system developed by the cited institution is based on cheap commercial UV lamps for aquariums. In September 2014, a new electronic for controlling the injection valve of this instrument was installed (the previous one had been faulting occasionally). On September 3, 2015, we installed a **flow controller** downstream the gas multi-position selection valve.

At the end of 2013 we began to perform occasional **tests of air tightness** to the dedicated **inlet lines of the GHG measurement systems** by capping the ends of the line, evacuating part of the air inside of the line and measuring the subsequent pressure increase rate. In May 2014, 7-micrometre **filters** were installed in all the dedicated inlet lines of the GHG measurement systems. In 2014, permanent **vents** were introduced downstream of all the pumps (to decrease the pump downstream pressure). In May 2014, we installed a system to evaporate quickly (by continuous high flow-rate flushing, using pumped free troposphere air) all the liquid water content of the flasks not being used at a given moment by the cryocoolers. In February 2015, electronic pressure sensors were installed in those vents and electronic temperature sensors were installed in the cryocooled baths (additionally to the thermometer used by the control system of each cryocooler) and in the ambient air of the two IZO GHG labs, and all their measurements acquired (still under development).

In December 2013, IZO was severely hit by lightning associated to severe thunderstorms. The **IZO GC-FID Dani was damaged**. The IZO GC-FID Varian has been our primary CH4 instrument since January 2014. During the first half of 2014 **we** repaired the GC Dani and **introduced many changes in it**: 1) use of a stainless steel dedicated ambient inlet line; 2) the carrier gas is N2 (instead of the synthetic air historically used at IZO); 3) a new injection valve was installed (Valco); 4) column oven at 69 ºC; 5) installation of a flow controller downstream the gas multi-position selection valve; 6) installation of a permanent vent downstream the dedicated pump and a low-flow vent downstream the dedicated cryotrap (and equalization of sample loop flushing times); and 7) substitution of the acquisition shielded wire.

At the beginning of February 2014, the **IZO NDIR Li-7000 broke down** (IZO primary CO2 instrument). We sent it to Germany for being repaired. From that date till middle May 2014, the IZO NDIR Li-6252 was used as IZO primary CO2 instrument. **When** the Li-7000 **returned repaired** (beginning of May 2014), **we introduced some changes** in its inlet system: 1) a vent was installed downstream of the dedicated pump and we removed the two solenoid valves of the ambient air inlet (V0 and V1 of Figure 1 of Gomez-Pelaez et al., 2011) and connected this line to a port of the MPV and the MFC1 to the outlet port of the MPV (the notation follows the cited figure); 2) after that date the data processing software discards 6 minutes of ambient air measurement every hour just after the measurement of the working standards (while the flask of the cryocooler is flushed). The same changes were applied to the Li-6252 measurement system on June 4, 2014.

During the first half of 2014 we introduced some **changes in the IZO GC-FID-ECD Varian**: 1) at the beginning of February 2014, a permanent vent downstream of the dedicated pump and a low-flow vent downstream of the dedicated cryotrap (and equalization of sample loop flushing times) were installed; 2) in June 2014, we installed a new sample-loop selection valve (of rotary type) instead of the 3-way solenoid valve that had been used previously (valve V4 of Figure 1 of Gomez-Pelaez et al., 2009), and two independent flow controllers downstream of the two outlets of this selection valve (instead of the previously used unique flow controller upstream of this valve).

We have developed software in Fortran 90 to process approximately in quasi-real time the raw data to obtain provisional mole fractions for the NDIR Li-6252, GC-ECD and RGA-3 (for the rest of the IZO GHG instruments such software was developed some years ago). We have developed scripts to load such quasi-real time data into a database **and** then such data **is graphically showed in IZO intranet pages** for early internal diagnostic (still under development).

We have developed software in Fortran 90 to compute very accurately ambient air mole fraction from raw data and the hierarchy of calibrations, **for the IZO secondary CO2** measurement system (based on a Li-6252, which was temporarily the IZO CO2 primary system during most of the first half of 2014) **and for the IZO GC-FID Varian measurement system** (this system has been the primary system for IZO CH4 since January 2014). The ambient air processing data scheme used for the IZO Li-6252 is very similar to that previously developed for the Li-7000 (described in Section 2 of Gomez-Pelaez et al., 2011). Also**, some small refinements have been introduced in the** cited **Li-7000 ambient air processing software** (i.e., for the mean parameters <a3/a2> and <a4> used in Eq. 2 of Gomez-Pelaez et al., 2011, the computation of the former is now performed dividing in -time interval- subsets the global set of calibrations –a different mean is used for each time interval-, whereas the later parameter is now considered as linearly dependent on temperature; small increase of the time period of ambient air measurement discarding every hour just after the measurement of the working standards,…).

We are purchasing the necessary material to introduce improvements in the dedicated inlet lines: 1) back-pressure regulators for the vents located downstream the pumps and rotameters for those vents; 2) needle valves to be used in low flow vents to be installed downstream the cryotraps; 3) glass flask cryotraps with Ultra-Torr connections; 4) secondary small stainless steel traps; 5) hermetic plugs for unused ports of the rotary Valco valves; 6) additional filters; and 7) high quality tubing for building GC sample loops.

3. Scale updates, recalibration of IZO laboratory standards at GAW CCL (NOAA), and accounting for the drift of one of the IZO CO laboratory standards

Table 1 shows the set of laboratory standards (prepared and calibrated by GAW CCLs) **used currently as IZO "primaries"**. All of them have been **recalibrated at NOAA during the second half of 2014 and the first half of 2015** (sent in two independent shipments not overlapping in time). However, one of the N2O/SF6 standards was purchased in 2014 (that written using underlined cursive in the table). **None of IZO laboratory standards have** significantly (in the statistical sense) **drifted along years, except one of the CO laboratory standards**.

Molecule	**Number of standards and serial numbers**	**¿Statistically significant drift?**	**Current scale used at IZO for in situ ambient measurements**	**Period of in situ ambient measurements**
CO2	**6** (CA06905, CA07421, CA02839, CA07969, CA06817, CA06800)	**NO**	WMO X2007 *****	1984-present
CH4	**3** (CA08201, CA06930, CA06932)	**NO**	NOAA-2004	1984-present $^{+}$
N2O	**6** (CA06739, CA06970, CA08203, CA06996, CA06964, *CB10914*)	**NO**	NOAA-2006A *****	2007-present
SF6	**6** (CA06739, CA06970, CA08203, CA06996, CA06964, *CB10914*)	**NO**	WMO X2014 *****	2007-present
CO	**5** (CA06768, CA06946, CA06988, CA06968, CA06978)	**NO except CA06946**	WMO X2004	2008-present $^{++}$

Table 1 – Set of laboratory standards used currently as IZO "primaries" for the different greenhouse gases (and carbon monoxide), drift assessment, current scale for ambient measurements, and period of in situ ambient air measurements. A red asterisk means that this scale has been implemented by us at IZO in 2015 in the way described in the main text. Note + : the data submitted to the WDCGG for the year 2014 has been obtained using a Varian-3800 GC-FID (for the previous year a Dani-3800 GC-FID was used). Note ++ : in 2015 the full CO time series has been reprocessed (and re-submitted to the WDCGG) taking into account the drift of one of the laboratory standards and the IZO internal recalibrations of the standards used in 2008.

A scale with a red asterisk means that this scale (the latest released by GAW CCL for this gas) has been implemented by us at IZO in 2015, in the way described as follows: 1) the mole fraction of each laboratory standard in this new WMO scale has been assigned as the mean (weighted in reproducibility in case the reproducibility of the GAW CCL has changed significantly along the years) of the CCL calibrations for such standard (for CO2, we have also taken into account the internal re-calibrations of old laboratory standards against our current laboratory standards); 2) all the previous IZO instrumental and working standard calibrations have been reprocessed taking into account the new mole fractions assigned to the IZO laboratory standards; 3) **all the previous ambient air measurements have been re-evaluated** using the new time series of instrumental responses and working standard mole fraction assignments, **and re-submitted to the WDCGG** (for CO2, this process has been performed only for the data period 2007-present).

Concerning **the CO drifting standard (CA06946)**, there is a statistically significant difference between the re-calibration performed by the CCL during the second half of 2014 and the original calibration performed by CCL at the beginning of 2006. However, the CO calibration results are provided by the CCL at present in the WMO X2014 scale. This scale has still unresolved problems of stability, and it is not recommended yet to perform the change to this new scale. Therefore, we have proceeded as follows for determining the drift rate of the drifting standard: 1) we continue using the original mole fractions for the 4 no-drifting standards (in scale X2004); 2) we have reprocessed all the previous IZO RGA-3 CO calibrations using the set of 4 no-drifting standards as calibration standards and the drifting standard as tank being calibrated in such calibrations. See the increment of mole fraction –above the original value assigned by the CCL- obtained for that standard along its lifetime in Figure 1. This figure also shows the least-square fit of these calibration results to a linear drift in time, the equation of such straight line and the coefficient of determination (R^2) of the fit. The drift rate of this laboratory standard is equal to 0.489 ppb/year. This result is consistent with the provisional re-calibration result obtained by the CCL.

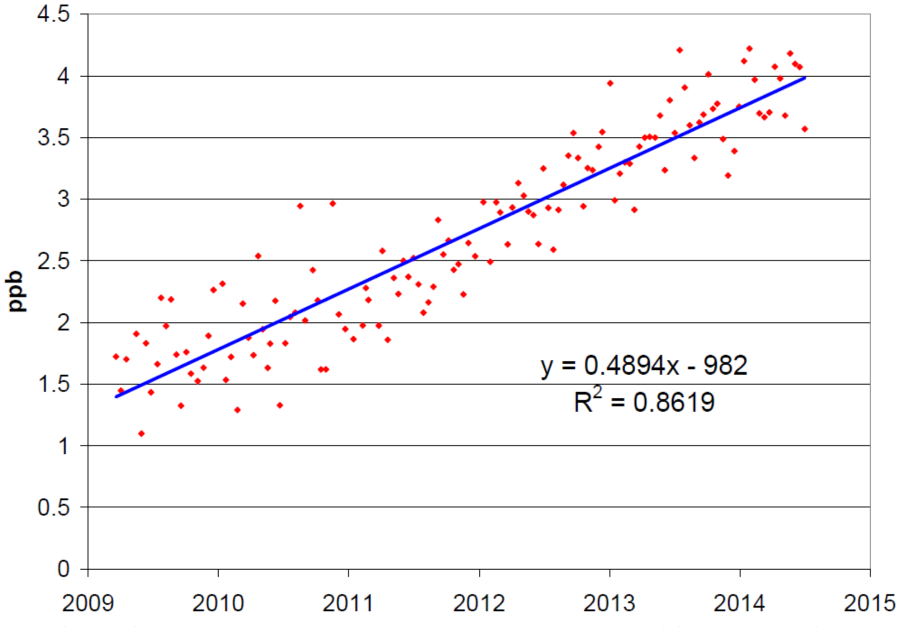

Figure 1 – Increment of mole fraction –above the original value assigned by the CCL- obtained for the IZO CO laboratory standard CA06946 along its lifetime from the bi-weekly RGA-3 calibrations performed at IZO (using as calibrators the 4 other non-drifting IZO CO laboratory standards).

The combined impact (new value minus old value; in absolute value) **of the scale updates** we have recently implemented **as well as** of the internal recalibrations of old laboratory standards, drift in one CO laboratory standard, slight data processing software modifications… **on the** new IZO CO2, N2O, SF6 and CO **time series re-submitted to the WDCGG** is: <= 0.04 ppm for CO2, <= 1.4 ppb for CO, <= 0.11 ppb for N2O, and <= 0.012 ppt for SF6 (where we have compared the monthly means to quantify the impact).

We add here **a note concerning the CO working standards used at Izaña observatory** (we fill and calibrate at IZO all the working standards used) **to complement** what was exposed in the first paragraph of page 790 of **Gomez-Pelaez et al. 2013**. We use 20-L cylinders obtained from Air Liquide Spain to contain the working standards of CO2, CH4, N2O, SF6 and CO. If we find that a CO2 working standard drifts too much along its lifetime of several months (i.e., total drift larger than 0.2 ppm), then, in the following, the corresponding cylinder is only used to create CO working standards (because the laboratory relative compatibility required by GAW for CO is much less stringent than for the greenhouse gases measured at IZO). Therefore, at IZO, the CO working standards are contained in the worst behaved IZO cylinders.

4. Aircraft campaign

After GGMT-2013 we finished adapting the IZO GHG in situ measurement systems to be able to measure also discrete samples collected on board aircrafts using a quasi automatic sampler (a Programmable Compressor Package –PCP- with a Programmable Flask Package –PFP-, both designed and routinely used by NOAA-ESRL-GMD-CCGG) and tested the sample extraction, distribution and measurement system. We participated in the MUSICA (project led by the Karlsruhe Institute of Technology) – AMISOC (project led by the National Institute of Aerospace Technique of Spain –INTA-) aircraft campaign: 7 scientific flights (using the INTA's research aircraft C-212) were carried out between 21th July and 1st August 2013 above the ocean to the south of IZO, freighting on board instrumentation of both projects (for the measurement of isotopes in water vapour and of aerosols).

We took the opportunity to install on board this aircraft by first time our quasi automatic air sampler (see Figure 2). In each flight, the sampler was used to take twelve air samples from different altitudes uniformly distributed from the 150 metres to the 6500 metres altitude levels. The greenhouse gases content of these samples was analysed latter at Izaña Observatory. We plan to publish a paper about these measurements in the near future.

Figure 2 – Left picture: quasi automatic air sampler installed on board the INTA´s aircraft. Right picture: group picture (crew and some of the technicians and scientists involved in this campaign) and aircraft.

5. Plumbing design for CRDS

We are purchasing a GHG CRDS for IZO. **Figure 3 shows a schematic of the plumbing design we have developed for the GHG CRDS we are going to install at IZO, which takes advantage of the fact that there are technical personnel at the station everyday**. We are going to **partially dry** the ambient air to be analysed by **using a flask immersed in a cold bath** (at around -30ºC). Two ambient inlets will be used for the CRDS: 1) one coming from one of the two IZO general inlets, and 2) a dedicated Synflex 1300 3/8" O.D. line coming from the top of the IZO tower. The CRDS lines coming from the IZO general inlet manifold and from the CRDS dedicated-inlet tee will be 1/4" O.D. There will be a cryocooled flask (with Ultra-Torr connections) for each of these lines. A solenoid 3-way valve will select the line in use (there will be alternation).

The laboratory standards and target gases will be connected to a rotary multi-position valve (MPV). **The laboratory standard cylinder valves will be usually close and only opened when performing a calibration** (this is probably beneficial to keep the mole fractions of the laboratory standards stable). The purpose of the solenoid valve located downstream of the MPV is to vent the gas coming from flushing the laboratory standard regulators before starting a calibration. In order to **get the same pressure in the inlet of the CRDS when measuring standards and ambient air, a needle valve will be used to decrease the pressure of the gas** coming from the MPV. In order to minimize the difference between the ambient pressure and the inlet pressure at the opening of the CRDS when measuring ambient air, a 3/8" O.D. Synflex 1300 line will be used for the CRDS dedicated inlet (with a length of around 25 metres). Anyway, the water vapour corrections will be determined using the water drop method (the error of these corrections will be negligible since ambient air will be quite dry after flowing through the cryotrap).

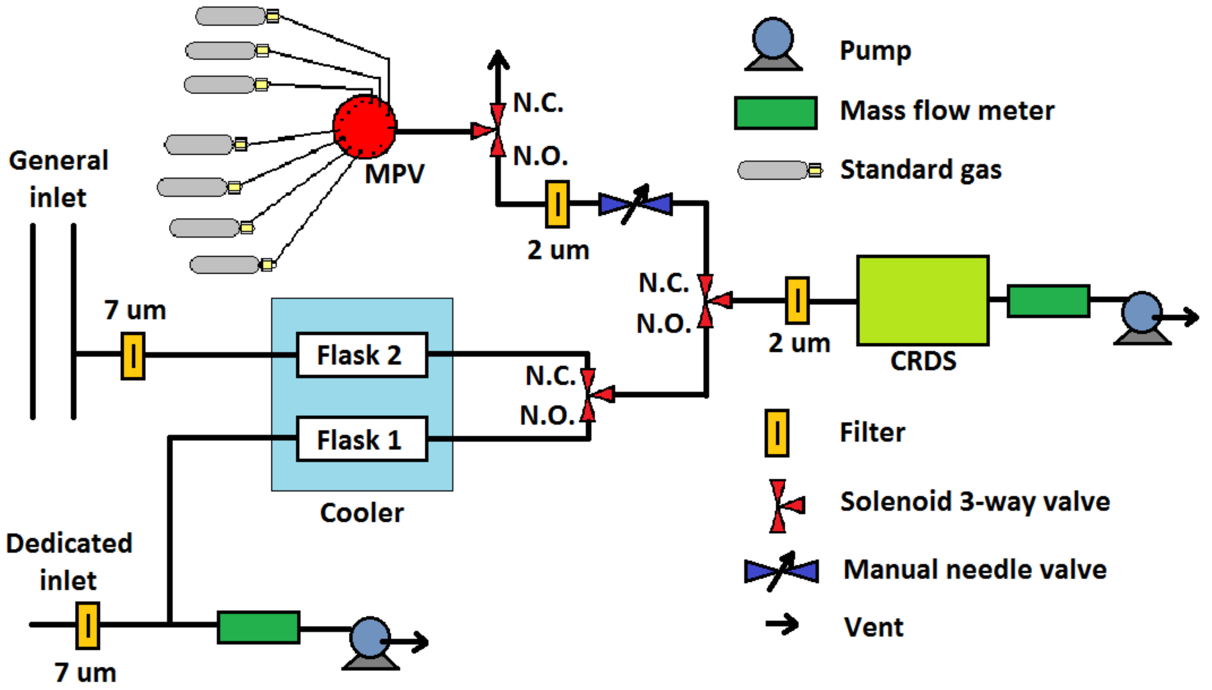

Figure 3 – Schematic of the plumbing design we have developed to install a CRDS next year at IZO.

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