TTorch Report

Title: ***Optimization of CH_4 and N_2O continuous measurements at Lampedusa ENEA station.***
Author: ***Florinda Artuso***

1. Purpose of the visit

The main aim of the visit to the Laboratoire des Sciences du Climat et de l'Environment (LSCE/IPSL), Gif-sur-Yvette CEDEX, France, is the optimization of CH_4 and N_2O continuous measurements at Lampedusa station in order to derive better source/sink scenarios in the Mediterranean area.

The recent increasing impact of CH_4 and N_2O to the global warming has been assessed by the last AR5 IPCC report (IPCC, 2007). Together with CO_2, CH_4 and N_2O are the principal long-lived greenhouse gases (GHGs) emitted by human activities. Observations of GHGs are essential for predicting their future trends and for quantifying human contribution to the observed build-up. For this purpose a network of globally distributed observing remote sites has been established by the World Meteorological Organization (WMO). Focussing on the Mediterranean basin the network includes the only GHG observation site located on Lampedusa island. Lampedusa has been selected for its geographical position that is particularly favourable for climate studies. Surrounded by the sea and scarcely inhabited, it is almost unperturbed by human activities and may be considered representative of a large area of the Mediterranean.

The station, active since 1997, is managed by the Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA). Monitoring of the main GHGs (CO_2, CH_4, N_2O, CFC-11, CFC-12) is carried out on a weekly basis and with continuous measurements. Since 2004 also several halocompounds (HCFC-22, HFC-134a, HCFC-141b, HCFC-142b and SF_6) are weekly monitored and from September 2007 halocarbons measurement program was extended to a number of halogenated trace species (CFC-113, CH_2Cl_2, $CHCl_3$, CH_3Cl, CH_3I, CH_3Br, CH_2Br_2, CCl_4, CH_3CCl_3, Halon-1301, Halon-1211). More details on the GHG monitoring program can be found in the literature (Artuso et al., 2007; Chamard et al., 2003; Artuso et al., 2009).Weekly CH_4 and N_2O data have been analyzed in Artuso et al. 2007 and in a recent work under revision (Artuso et al., 2010). In contrast CH_4 and N_2O continuous data have never been published because of their poor quality. On-line time series shows high short term variability (±30 ppb for CH_4 and ±4 ppb for N_2O during a month) and long gap periods due to drawbacks in the experimental apparatus. High precise and accurate measurements are necessary for an integration of GHG data on global scale and for regional fluxes modelling. To reach this goal within the GAW network the scientists present at the 14th WMO/IAEA Meeting of Experts on Carrbon Dioxide, Other GHGs and related tracers measurement techniques recommended an inter-laboratory comparability of ±2 ppb for CH_4 and of ±0.1 ppb for N_2O (WMO, 2007). Due to the poor quality of our continuous CH_4 and N_2O time series, at present the data cannot be used in the models for estimating regional emissions.

The LSCE RAMCES group has a long expertise on GHG monitoring and is worldwide recognized as a laboratory of excellence in this field. The laboratory produces high quality records of the main climate impacting species (CO_2, CO, CH_4, N_2O, SF_6) and run a complex monitoring program worldwide distributed. A scheme of the LSCE GHG global monitoring program is reported in Figure 1 while Figure 2 shows a zoom at the national scale.

Purpose of the visit to LSCE is to get information on the protocols used for CH_4 and N_2O measurements and quality control in order to harmonize our records and reach a good intercomparability between the labs . The visit is also aimed to consolidate the collaboration, already established within some European projects (CarboEurope, IMECC, ICOS), between our lab and the host institution.
The optimization of continuous GHG measurements at Lampedusa is aimed to contribute to the monitoring network in Southern Europe and to support inverse modeling top-down emission estimate.

2. Description of the work

25.07.10-Arrival to Paris.

26.07.10-Visit to the LSCE laboratory at Gif sur Yvette, Paris.
RAMCES is the French Network of Atmospheric Greenhouse Gas Monitoring (see Fig.1). The LSCE RAMCES laboratory sited at Gif sur Yvette, Paris, (48°43'N, 02°09'E, 20 m asl) is equipped with instruments dedicated to in-situ and flask GHG measurements. The lab includes also a flask storage room where flasks within the RAMCES network are first prepared (preconditioned and evacuated) before delivering to the sampling sites and finally collected. Within the flask sampling program about 2200 flasks/year are measured at LSCE. The program includes 12 fixed surface sites and 5 airborne sites.
The RAMCES CO_2 and Radon-222 monitoring program started in 1980 at the Amsterdam Island observatory and was extended at Mace Head, Ireland, in 1992 and at two further sites in France (Gif-sur-Yvette and Puy de Dome, 2001). In addition, a flask sampling program started at LSCE in 1996. Table 1. summarizes the flask sampling sites of RAMCES.

Table 1: Flask sampling sites of RAMCES.

Site	Latitude	Longitude	Alt. (m)	Country	Start
Amsterdam Isl	37°48'S	77°32'E	70	France	1996
Mace Head	53°20'N	9°54'W	25	Ireland	1996
Puy de Dôme	45°46'N	2°58'E	1465	France	2001
Orléans	47°50'N	2°30'E	100-3000	France	1996
Tver	56°27'N	32°55'E	100-3000	Russia	1998
Hegyatsal	46°57'N	16°39'E	100-3000	Hungary	2001
Griffin [1]	56°33'N	2°59'W	100-3000	Scotland	2001
Ile Grande	48°48'N	3°35'W	20	France	1998
Tromelin	15°54' S	54°31'E	10	France	1998
Cape Grim	40°41'S	144°41'E	164	Australia	1998
Begur	41°58'N	3°14'E	13	Spain	2000
Finokalia	35°19'N	25°40'E	150	Greece	2001
Hanle	32°47'N	78°58'E	4517	India	2000
Pic du Midi	42°56'N	0°08'E	2877	France	2001
Marion Dufres	Indian Ocean		20		1996

At Gif sur Yvette LSCE lab the samples are analyzed for CO_2 isotopes ($\delta^{13}C$ and $\delta^{18}O$) and for CO_2, CH_4, N_2O, SF_6, CO, H_2 and Radon-222 mixing ratios.
The following analyzing facilities are present (see also Table 2):
1) **CO_2** measurements. The lab is equipped with five PICARRO analyzers, a NDIR LOFLO-Licor 6251, a CARIBOU-Licor 6252 analyzer and a multi GC system (see below). The EnviroSense 3000i analyzers, marked by Picarro Inc., are a new generation of instruments based on the cavity ring-down spectroscopy (CRDS)

principle and designed for high precise measurements of CO_2, CH_4 and H_2O. LSCE is testing EnviroSense analyzers since June 2007.
2) Analysis of **CO_2**, **CH_4**, **N_2O**, **SF_6**. A multi GC system HP6890N (Agilent Technologies). The GC is equipped with two parallel measurement lines: a) a line dedicated to CH_4 and CO_2 measurements equipped with a FID detector and a catalyst. b) The second line, for N_2O and SF_6 detection, has an ECD detector. The detailed configuration of the GC is described below (see Puy de Dome GC system description).
3) A PP1 GC system (in series with the GC HP6890) for **CO**, **H_2** measurements.
4) A mass spectrometer for the analysis of CO_2 isotopes (**$\delta^{13}C$** and **$\delta^{18}O$**).
5) A non conventional analyzer for measurements of **Radon-222**.
6) A meteo tower for measurements of the main meteorological parameters (wind speed and direction, temperature, pressure, humidity).

Table 2: In-situ measurements at LSCE.

Site	**Country**	**Latitude**	**Longitude**	Alt. (m asl)	**Measurements**	**Instruments**	**Start time**
Gif-sur Yvette	France	48°43'N	02°09'E	20	CO_2 CO_2 CO_2 CO_2, CH4, N_2O, SF_6 CO, H_2 Rn-222 Meteo param.	LOFLO CARIBOU PICARRO Multi-GC (Agilent) PP1 GC	2005-… 2006-… 2007-… 2001-… 2006-… 2001-…

27-28.07.10-Visit to Puy de Dôme Station
LSCE GHG monitoring program at Puy de Dôme station was activated in 2001 for continuous measurements of CO_2 and Radon-222. The station is sited in the heart of France, in the region of Auvergne, near the city of Clermont-Ferrant. Puy de Dome is part of the volcanic Chain of Puys. The volcanos are inactive since more than 8000 years ago. The station is sited at 1465 m asl and is run by LSCE for CO_2 and Rn-222 measurements since 2001. Data of CH_4, CO_2, N_2O, SF_6 mixing ratios are also recorded since 2007 with a GC HP6890 (Agilent Technologies). Recently the measurement line has been upgraded by a new GC system HP6890N. Automation and the real-time data transmission of in-situ measurements is still in progress. Table 3 summarizes the in-situ measurements at Puy de Dome.

Table 3: In-situ measurements at Puy de Dome.

Site	Country	Latitude	Longitude	Alt. (m asl)	Measurements	Instruments	Start time
Puy de Dôme	France	45°46'N	02°57'E	1465	CO_2 Rn-222 CH_4, CO_2, N_2O, SF_6	Licor GC 6890 GC 6890N	2001-… 2001-… 2007-… 2010-…

The visit at the Station has been focused on a fruitful discussion about GC configuration, measurement methods and data elaboration.
Back to Paris.

29-30.07.10- LSCE laboratory at Gif sur Yvette, Paris.
-Description of the main LSCE GHG monitoring programs. In particular the discussion has been focused on the LSCE observation sites in Finokalia (35°19'N, 25°40'E, 150 m asl, Greece) and Lamto (06° 13’ N, 05°01W, 100 m asl, Ivory Coast,

Africa). Since 2001 a flask sampling program has been started by LSCE in Finokalia, on the Island of Crete in the Mediterranean. In-situ continuous measurements are planned for the near future. Lamto is an observing site established by LSCE in 2008 within the project CarboAfrica and located at 100 m asl on the Ivory Coast. Continuous measurements of CO_2, CH_4 and H_2O are recorded by an EnviroSense Picarro Analyzer.

-Definition of a strategy of data quality control.

-Presentation of Lampedusa station to the LSCE group.

-Final discussion about future collaborations and projected publications.

31.07.10-Back to Italy.

3. Description of the main results obtained

3.1 Comparison of GC configurations and experimental procedures for N_2O and CH_4 analysis

With the aim to harmonize our measurement lines and to improve the precision of our system a comparison of the GC configuration, measurements and data analysis used at LSCE and at ENEA has been carried out during the visit.

Measurements of N_2O and CH_4 at our lab (ENEA, Lampedusa) and at the visited LSCE labs (Gif-sur-Yvette, Puy de Dome) are both performed with a GC 6890 (or the advanced model 6890N), Agilent Technologies, equipped with an electron-capture detector (μECD) and a flame ionization detector (FID). Both GC lines use N_2 and Ar/CH4 as carrier gases. Nevertheless the GC configurations present marked dissimilarities. The ENEA GC has two parallel lines, one for CH_4 detection (FID) and the other one for N_2O, CFC-11 and CFC-12 (μECD). The air is sampled by means of an oil free piston pump and then flows through a magnesium perchlorate water vapor trap. The FID line has a 0.5 ml loop for the injection, a 25 m x 0.53 mm (20 μm film thickness) Poraplot Q capillary column. Separation of methane is achieved by maintaining the column at 50 °C and the CH_4 retention time is about 1.75 min. The ECD line is equipped with a 25 ml loop and an Altech Porasil B packed column. The column temperature is maintained at 50°C during analysis. Before each injection the loop is flushed for about 2 minutes at 50 cc min^{-1}. N_2O, CFC-12 and CFC-11 elute at 3.02, 4.92 and 14.55 minutes respectively.

At LSCE the sampled ambient air is dehydrated by a cryogenic system consisting in an ethanol bath maintained at -60°C (Thermo NESLAB CC-65). The FID line is fed by N_2 5.0 (purity ≥ 99.999% vol) and equipped with a packed molecular sieve column Hayesep-Q, 12’x3/16’’SS, 80-90 mesh and by a catalyst for the detection of CO_2. CH_4 and CO_2 retention times are respectively 2.42 and 2.95 min. The μECD carrier gas is a mixture of Ar/CH_4 (5%) purified by a filter AERONEX GateKeeper 35KF. The sample first flows through a pre-column (Hayesep-Q 4’x3/16’’SS), from which N_2O and SF_6 elute after around 1 minute. They are then directed to the analytical column (Haysep-Q, 6’x 3/16’’ OD, 80/100). At this point the pre-column is back-flushed, avoiding contaminants passing through the ECD and reducing analysis time. With this configuration, N_2O and SF_6 are respectively eluted 3.20 and 3.66 minutes after the sample’s injection.

Main differences between the ENEA and LSCE GC systems:

1) Moisture trap system. A sodium perchlorate trap is used at ENEA while an ethanol bath at -60°C is used at LSCE. Drawbacks of the sodium perchlorate trap: when the trap is saturated the salts melt and can contaminate the sampling lines.

2) At LSCE the FID line is fed by a cylinder of certified high purity N_2 while at ENEA the N_2 carrier source is a generator. The lowest quality of the carrier may increase the measurement noise.
3) Catalyst for CO_2 measurements. The LSCE system is equipped with a methanator which allows the simultaneous detection of CO_2 and CH_4. The ENEA FID line is able to measure only CH_4.
4) Columns and pre-columns. The use of a pre-column in the N_2O/SF_6 LSCE line reduces noteworthy the analysis time. The possibility of changing our GC/ECD column in order to substitute CFCs measurements with SF_6 will be evaluated. At present SF_6 is only weekly monitored at ENEA and measured in Rome with a GC-MS system, that in comparison with the GC-ECD is less sensitive to the detection of SF_6.
5) Retention and sequence times. The shorter retention times of the species analyzed at LSCE allow to run a measurement every 5 minutes while at ENEA our records have a frequency of about 16 minutes. Shorter analysis times permit to record higher frequency data and limit the errors due to the influence of ambient temperature and pressure variations.

3.2 Data quality control.

A strategy to evaluate and improve the precision, repeatability and accuracy of our measurement system has been defined during the visit at LSCE. To reach this target a comparison of LSCE and ENEA data has been first carried out. Figures 3 and 4 report N_2O continuous data recorded at Lampedusa and Gif-sur-Yvette LSCE labs respectively during one month. Figure 4 shows also the afternoon data (between 16.00 and 20.00 UTC) at Gif. These data are more representative of the background conditions because are less affected by the local pollution sources (i.e. traffic, influence of the boundary layer height etc.). Afternoon N_2O data at Gif have a standard deviation (std) of 0.5 ppb during one month (July 2010). In contrast Lampedusa data show a higher variability. The std during December 2009 is 1.9 ppb, almost 4 times higher than the expected one.

In order to achieve a better precision, the reproducibility and long-term stability of the measurement system have to be checked and optimized.

For this reason a protocol for data quality control has been defined after an inter-laboratory comparison of the following items.

1) Sequence of analysis and calibration strategy.

Comparison between ENEA and LSCE.

ENEA: Two standard mixtures provided by the Climate Monitoring and Diagnostic Laboratory/National Oceanic and Atmospheric Administration, (CMDL/NOAA), were used before 2009 while during the last year a third standard is used for the calibration line. The analysis sequence brackets measurements of the primary standards with the air sample (i.e. ST1, ST2, sample, ST3, sample, ST1, sample, …).

LSCE: Two working standards (WH and WL) are used for calibration. Every 3 month, the working standards are calibrated against 2 international standards, which are provided by NOAA CMDL (Boulder, US) that constitute the primary scale. A third NOAA's standard is used as a target (WT) , in the same way than for the working standards. The WT is used as a tracer for data quality control (see below). Sequence of analysis at LSCE alternates measurements of the working standards, WT and samples (x) as follows: WL, WT, WH, x1, x2, x3, x4, WL, WT, WH etc.

2) Repeatability (short term stability) of our system has to be checked by reproducing multiple measurements on the primary standards.

2)Optimization of the calibration frequency.

To define the best calibration frequency it is recommended to analyse the evolution of the reproducibility of the species during a period of 24 hours. The test works as follows: 3 standards (ST1, ST2, ST3) are injected consecutively during 24 hours. ST2 is determined during the whole period of analysis using ST1 and ST3 for calibration.ST2 mixing ratios are calculated varying the period of analysis between ST1 and ST3 and finally plotted vs. the calibration frequency. Results from this test at LSCE showed that CO_2 and N_2O are sensitive to the variation of the calibration frequency and for this reason it is recommended to inject the standards at least once per hour.

3) Long term stability control.

To check the quality and control the stability of the measurements at LSCE, a so-called "target gas" (WT) is injected every hour. Its concentration is calculated exactly in the same way as real samples. The long term control of the accuracy of measurements is performed by checking the concentration variations, for every species, of the WT. The precision is defined as the std of the concentration of the target gas (WT) calculated during 24 hours. The precision depends upon the intrinsic parameters of the measurement system and is variable in the time.

Target measurements at Gif-sur-Yvette during one month are shown in Figure 5. Precisions of the chromatographic systems at LSCE are typically <0.1 ppm, <1.2 ppb, <0.3 ppb and <0.07 ppt for CO_2, CH_4, N_2O, and SF_6 respectively.

The same test is advised to check the reproducibility of the ENEA GC system and the use of a target standard is recommended for ensuring the long-term quality control of data.

4) Sensitivity to T and P variations.

The efficiency and resolution of a GC separation are directly related to temperature (T) and pressure (P). T fluctuations are responsible of fast variations while the P is responsible of the long term drift. A test to check the influence of P and T during a period of 4 days is planned for improving the precision of the measurements. A climatisation system could be installed in case results from the test indicate that the influence of T and P is elevated.

4. Future collaboration with host Institution

The visit to LSCE was also aimed to reinforce the cooperation between our lab and the host Institution. A collaboration has been already established within the previous European projects Aerocarb and CarboEurope and it is still in progress within the infrastructure networks IMECC and ICOS. The visit consolidated such collaborations and plans for future works and information exchanges have been established. In particular, with the aim to contribute to the scarce continuous GHG monitoring network in Southern Europe, to support inverse modeling top-down emission estimate and to verify the development of GHG trends in Europe in relation to emission reduction measures under the Kyoto Protocol, a comparison between GHG data series from Lampedusa (ENEA) and Finokalia and Lamto (LSCE) observation sites has been planned.

5. Projected publications resulting from the grant

Two items have been identified for possible common publications:

1) Combined study of CH_4 data series from Lampedusa and Lamto with inverse modelling for the evaluation of CH_4 emissions from North Africa gas/petroleum pipelines.

2) Comparison of GHGs (CO_2, CH_4, N_2O) time series between Lampedusa and Finokalia to evaluate regional sources/sinks in the Mediterranean area.

Acknowledgements

Dr. Martina Schmidt is warmly acknowledged for her precious suggestions and availability during the whole host period. I also thank Dr. Philippe Ciais and Dr. Michel Ramonet for the hospitality at IPSL/LSCE labs.

I gratefully thank Dr. Alex Vermeulen for the information provided on the TTorch project.

References

Artuso F., Chamard P., Piacentino S., di Sarra A., Meloni D., Monteleone F., Sferlazzo D., Thiery F., 2007. Atmospheric methane in the Mediterranean: analysis of measurements at the island of Lampedusa during 1995-2005. Atmospheric Environment, 41, 3877-3888.

Artuso F., Chamard P., Piacentino S., Sferlazzo D., De Silvestri L., di Sarra A., Meloni D., Monteleone F., 2009. Influence of transport and trends in atmospheric CO_2 at Lampedusa. Atmospheric Environment, vol.43, 19, 3044-3051.

Artuso F., Chamard P., Chiavarini S., di Sarra A., Meloni D., Piacentino S., Sferlazzo D.M., 2010. Tropospheric halocompounds and N2O monitored at a remote site in the Mediterranean, Atmospheric Environment, under revision.

Chamard P., Thiery F., di Sarra A., Ciattaglia L., De Silvestri L., Grigioni P., Monteleone F., Piacentino S., 2003. Interannual variability of atmospheric CO_2 in the Mediterranean: measurements at the island of Lampedusa. Tellus 55B, 83-93.

Intergovernmental Panel on Climate Change (IPCC), Contribution of Working Group I to the Fourth Assessment Report 2007. Forster.P., V. Ramaswamy, P.Artaxo, T.Berntsen, R.Betts, D.W. Fahey, J.Haywood, J.Lean, D.C. Lowe, G. Myhre, Jnganga, R. Prinn,G. Raga, M. Schulz and R.Van Dorland, 2007;Changes in Atmospheric Constituents and in Radiative Forcing. In: Climate Change 2007: The Physical Science Basis. S. Solomon et al. Eds. (Cambridge Univ. Press, Cambridge, UK 2007).

World Meteorological Organization Global Atmosphere Watch No. 186, 2007. Report of the 14th WMO/IAEA Meeting of Experts on CO_2 concentration and related tracers measurement techniques. Helsinki, Finland, 10-13 September.

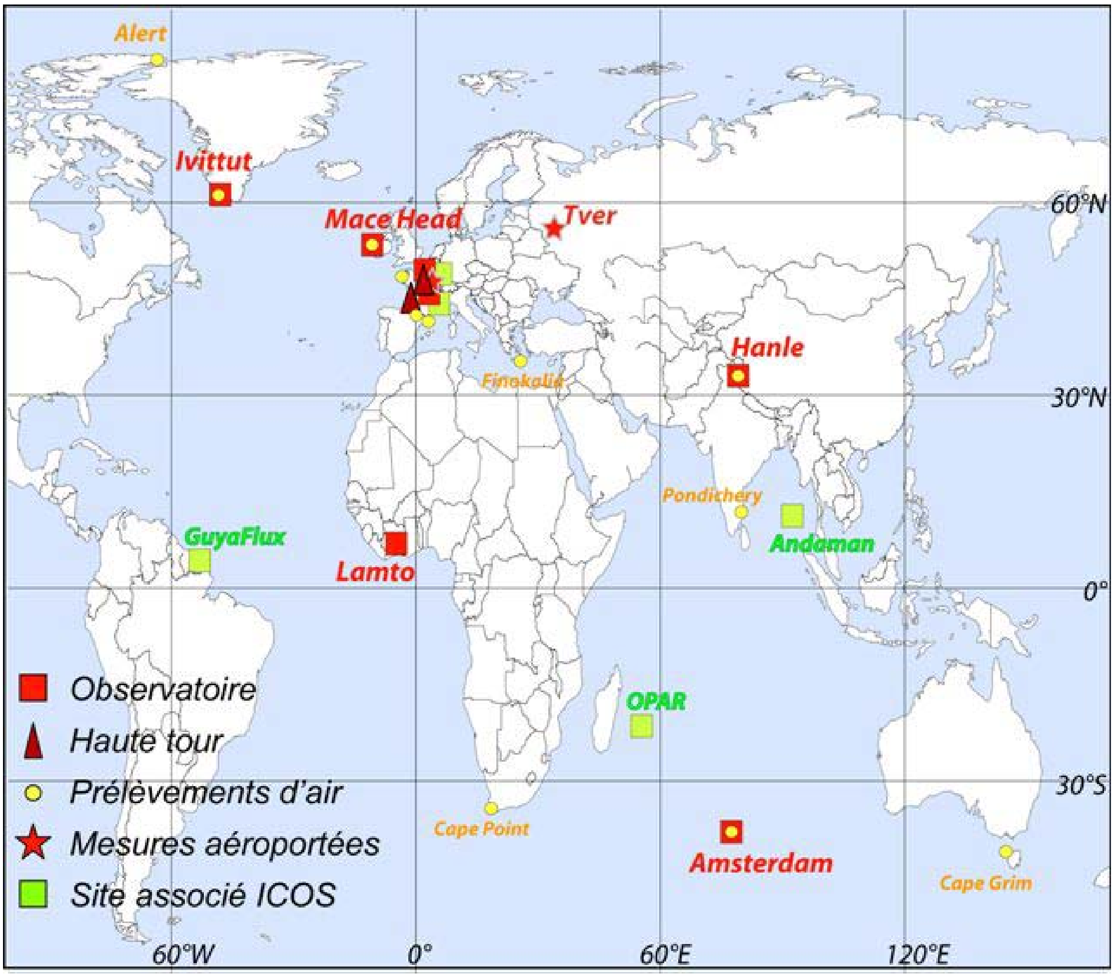


Figure 1. RAMCES flask sampling and in-situ measurement network.

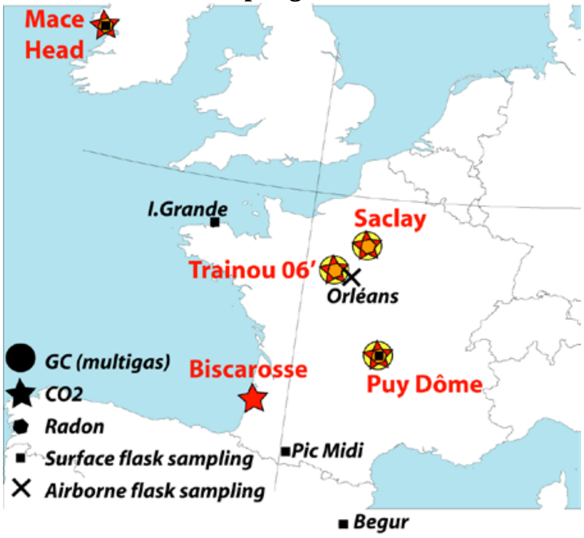


Figure 2. RAMCES National sampling and measurement network.

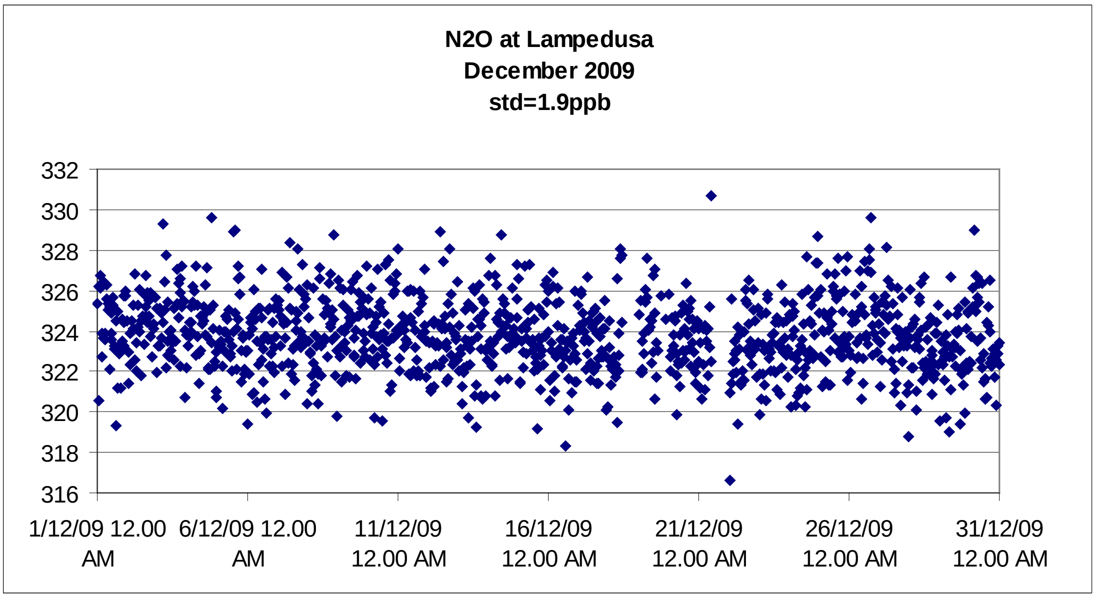


Figure 3. N_2O at Lampedusa during December 2009. All data are reported.

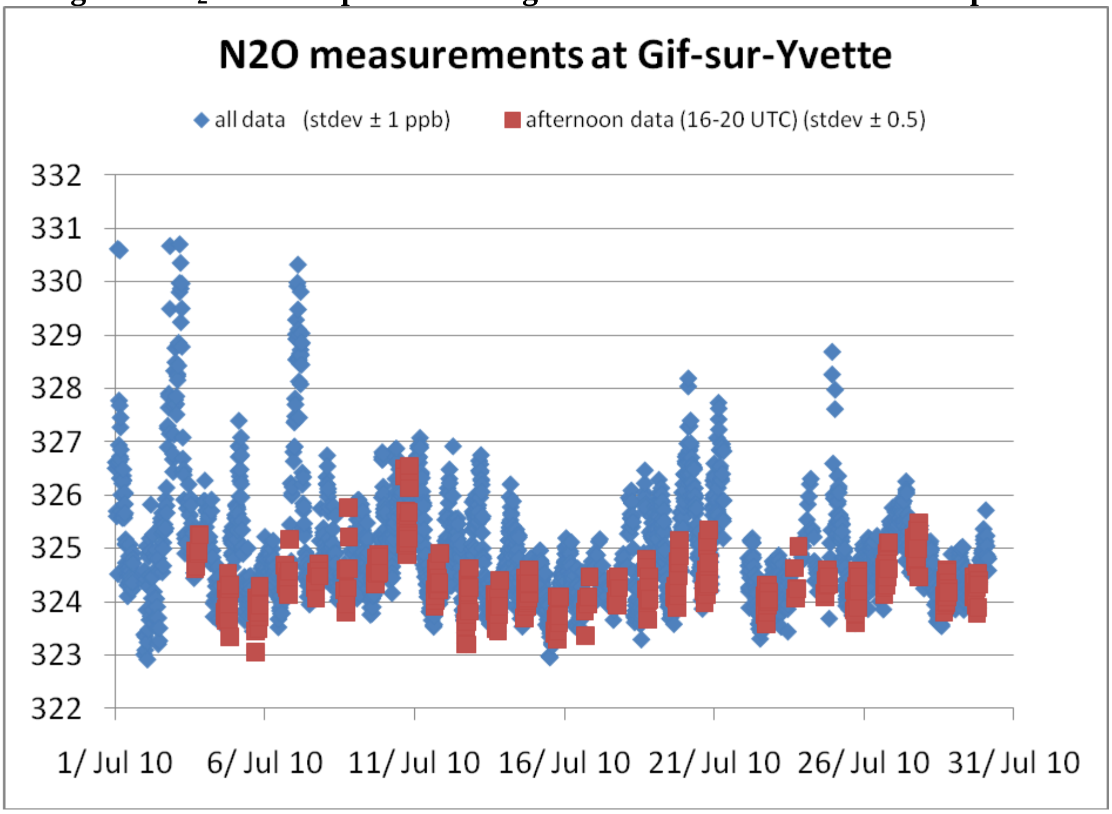


Figure 4. N_2O data at Gif-sur-Yvette. All and afternoon data are reported.

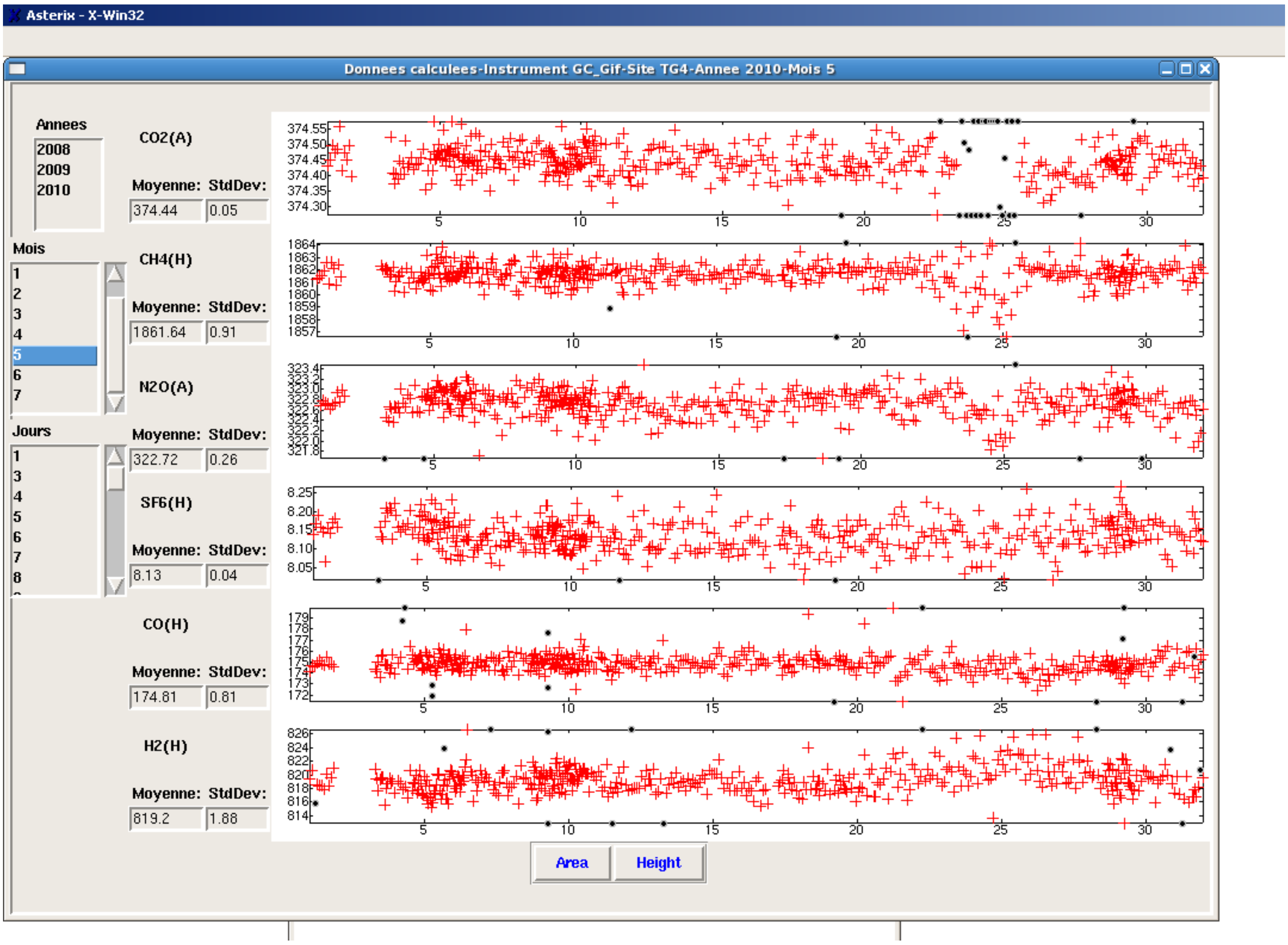


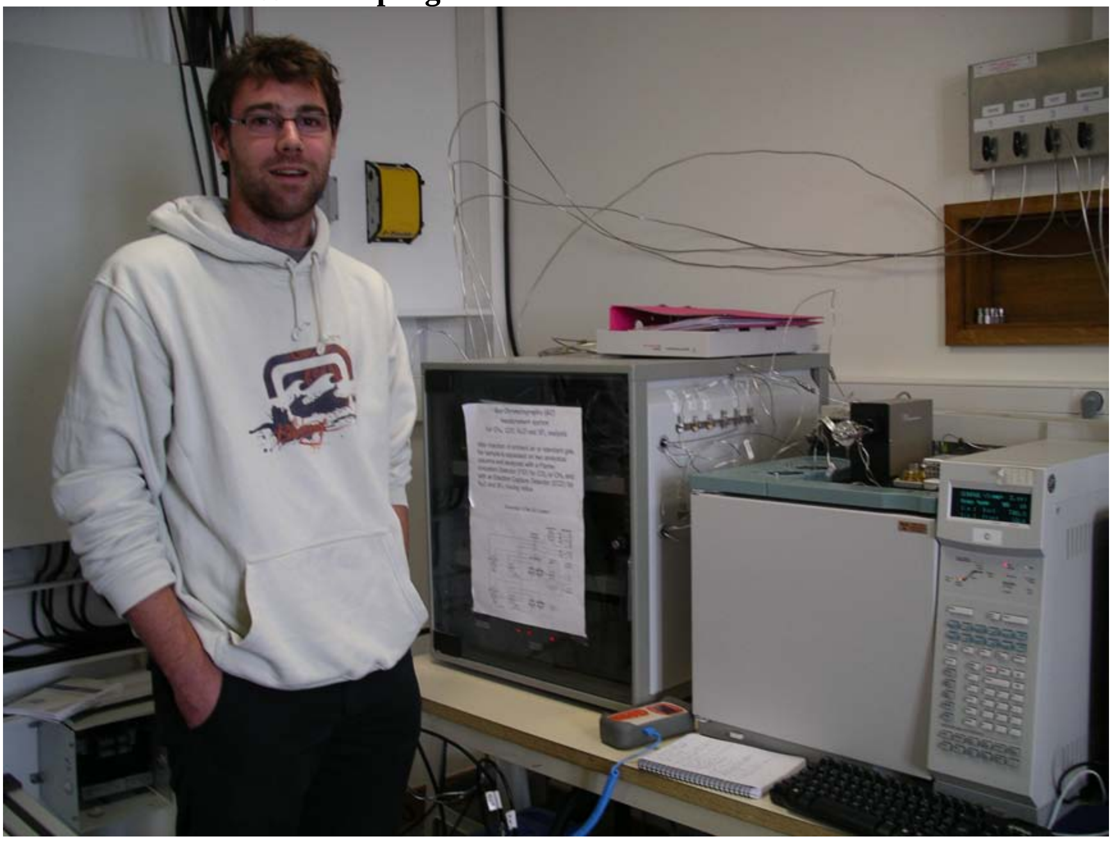
Figure 5. Target measurements at Gif-sur-Yvette May 2010-07-30

Pictures of the visit

Puy de Dome Station

Florinda and Martina on the roof of Puy de Dome station

Work in progress at Put the Dome Station…



Morgan Lopez and the GC at Puy de Dome

Florinda and Morgan at Puy the Dome

The LSCE laboratory entrance at Gif sur Yvette, Paris.

The LSCE Picarro analyzer room at Gif sur Yvette.