Final Report

MATAGRO – Monitoring of Atmospheric Tracers in Antarctica with Ground-based Observation

The main objectives stated in the work plan of the MATAGRO project were accomplished; namely: i) installation in Antarctic region of new spectrometric instrumentation for the automatic and unattended monitoring of the ozonesphere; ii) re-analysis of more than 10 years of data measured with the old spectrometric system at the Mario Zucchelli Station (MZS); iii) formation of graduate and master students in the spectral analysis with the Differential Optical Absorption Spectroscopy (DOAS) technique and inversion methods to retrieve total column and vertical distributions of atmospheric tracers such as nitrogen dioxide (NO2), ozone (O3) and bromine oxide (BrO). The activities in Polar Regions resulted in the participation of the project PI in four Italian Antarctic expeditions, which was possible only thanks the collaboration with the ISAC institute, taking advantage of the logistic coordination of the Italian Project for Antarctic Research. Thanks also to the support of the Portuguese polar program (PROPOLAR), MATAGRO was the first Portuguese project to establish activities in Antarctica in the field of atmospheric sciences. In the PROPOLAR website (http://www.propolar.org/matagro.html) the activities carried out within the MATAGRO project during the Antarctic expeditions were detailed described in almost real time. In the following the complete description of the activities developed within the MATAGRO are deeply described and explained.

During the first year of execution of the project one of the main results obtained is the participation (December 2011/January 2012) to the XXVII Italian Antarctic Expeditions at the Mario Zucchelli Station (MZS) (Figure 1).

Figure 1 – Mario Zucchelli Station – MZS

Unfortunately, during the participation to the expedition it was not possible to install the new Spectrometer (GASCOD/NG1-SPATRAM/MZS) at MZS since the equipment, even already funded and setup under previous PNRA (National Project for Antarctic Researches – Italy) projects, had to be deeply updated in order to be able to perform trustful spectral measurements in unattended and automatic mode in remote location as the Antarctic station. In particular, the electronic control unit was updated with a new CPU and mainboard (the old NOVA 7892 was replaced with a NOVA945GSE) and management logic that forced the re-wiring of the electric connections. Also the mechanical optical unit was upgraded installing: a new shutter type ensuring more than 10 MShuts (10 million of measurements - the old shutter system was limited to 1 million), a new device for the neutral density filter avoiding for the saturation of the CCD sensor, and others details were updated. The MIGE device has been slightly modified in order to be usable in extreme weather conditions adding temperature sensors, heaters and fan avoiding the formation of ice and of water vapor respectively, the external connections are now water proof. A new quartz dome has been adopted allowing for measurements in the UV spectral range. Only one of the foreseen 2 MIGE is setup also due to administrative problems that will be solved in a short time in order to proceed also with the setup of the next one. In order to ensure the possibility to carry out measurements to be compared directly with the ones obtained with the old GASCOD instrument, a new input device had been setup. The VELOD (Vertical Looking Device), already developed and used at the CGE, was modified for the Antarctic regions. The instrument was aligned and calibrated with spectral and halogen calibrated lamps. All these works started immediately after the approval of the proposal, but they lead to a delay that made impossible to send the instrument in Antarctica for the expedition 2011/12, since the material should had to be ready in July. In addition, the development of the new devices required the acquisitions of different types of stepper motors, sensors and other material from different provider of mechanical and electrical components. The already planned participation to the XXVII expedition was really useful since it was possible to make an extraordinary maintenance to the GASCOD instrument (the last was during the 2000/2001 expedition). Furthermore, a new device was installed for the management of the equipment and finally the location for the SPATRAM/MZS has been selected and prepared to receive the equipment in the already confirmed 2012/13 expedition. The participation to the Ant. Exp. resulted also in the contribution of the PI in an interview for the National Geographic

(http://www.nationalgeographic.it/viaggi-avventure/2011/12/09/video/video_dai_gas_minori_al_buco_nell_ozono-728832/1/)

The GASCOD/SPATRAM/DC, to be installed at the Dome Concordia Station, also had some delay in the adaptation to the Antarctic conditions, also because the Italian project (already approved in 2008/2009) suffered delay also. The scientific objectives in the first year of the project were really satisfactory, since the full dataset of the spectral data obtained with GASCOD during the period 1996-2009, was re-analyzed with a modified version of the software tool previously utilized. The uncertainties range from 4% up to 8% for O3 and from 3% tup o 6% for NO2. The peculiar features of the seasonal variation of O3 (i.e. during the 'Ozone Hole' periods (mid-August to mid-October) and NO2 total columns (i.e. the normal decreasing during the austral fall and the irregular growing towards the spring months) are clearly identified. For the first time, the NO2 total columns values, obtained with the GASCOD installed at MZS, were compared with the data obtained with satellite borne equipments (SCIAMACHY, GOME and OMI). The best fits of the GASCOD datasets over the different satellites time series give satisfactory results presenting determination coefficients in the range 0.88 ~ 0.93 for the GASCOD/SCIAMACHY and GASCOD/GOME comparisons. For the OMI comparison R is quite low (0.64 and 0.68 for AM and PM series respectively). This last aspect can be mainly due to the fact that the algorithms used by OMI in the calculation of the NO2 Air Mass Factor (AMF - the parameter allowing for the determination of the NO2 VCD from the output of the DOAS processing) take into account the seasonal variation of the NO2 vertical profile Further studies are required for a better

characterization of the GASCOD/OMI comparison. In addition, the Intercomparison of nitrogen dioxide (NO2) vertical profiles, derived from the satellite based HALogen Occultation Experiment (HALOE) measurements and from GASCOD were done for the first time, showing a good agreement presenting the same features in terms of magnitude, profile structure, and temporal variations.

Furthermore, studies on the radiative transfer models lead to improvements in the algorithms used for the computation of the geometrical factor for the retrieval of vertical columns and vertical profiles of atmospheric compounds.

During the second year of execution of the MATAGRO project, after the participation (December 2011/January2012) to the XXVII Italian Antarctic Expeditions at the Mario Zucchelli Station (MZS), most of the efforts were dedicated to the preparation of the GASCOD/NG1-SPATRAM/MZS system to the installation at MZS. These activities required 2 trips in Italy in order to: i) finish the upgrading and test of the instrument; ii) packing the instrument for its journey to Antarctica (started in September 2012).The new system was installed in Antarctica during the participation of the PI´s project to the XXVIII Italian Antarctic Expedition (January -February 2013). In Figure 2 the setup of the new instrument at MZS.

Figure 2 – SPATRAM MZS installed at MZS

Although the instrument was tested and prepared for the installation, at the arrival in Antarctica, mechanical, optical and electronic problems arise. Practically, once more the optical alignment and calibration of the spectrometer had to be performed. Some troubles in the electronic unit managing the optical and mechanical unit had to be solved. In addition, mechanical components had to be setup in the workshop of the station in order to install on the roof of the container the VELOD optical device for the capture of the radiation to be carried in the spectrometer main body with an optic fiber. Extra works were also done with the purpose of allowing the instrument to be time-synchronized with satellites: a GPS was connected to the instrument to UBS port and software was developed to allow the instrument to communicate with the GPS. We had the possibility to control the instrument with an internet connection

provided by the logistic of the station till the mid of March experiencing that the instrument was working as expected; after the 15 of March all the connections were closed. The participation to the XXVIII expedition allows for the possibility to download and process the data acquired by the ´old´ GASCOD spectrometer carried out during 2012 and to verify the goodness of the of the new devices installed during the previous expedition. The new data were processed and analyzed and the full dataset (1996-2012) was used for a deep comparison with satellite data (GOME, GOME2, OMI SCIAMACHY). A similar approach was already done and the presentation of the results was done in August at the IRS symposium 2012 in Berlin and published in AIP Conference proc. (ISI indexed). In the IRS2012 work the period was limited to 2001-2008 and the data of the GOME 2 were not available. The new results were presented in September 2013 at the SPIE conference in Dresden (Germany).

The activities of the third year of the MATAGRO project developed along different lines of research. First of all, thanks to the participation of the PI of the project to the XXIX Italian Antarctic expedition it was possible to check the conditions of the GASCOD/NG1-SPATRAM/MZS system installed during the previous expedition. The instruments worked for the whole austral autumn period when the station is closed and unmanned, but the data acquisition, stop in the middle of June. At the arrival to the station the system was found locked in the booting process probably to i) the low temperatures suffered during the winter (the shelter where the instrument is installed reached -35ºC) ii) the problem with the GPS connected to the instrument aiming to furnish signal for the time synchronization of the PC clock. The instrument has been restarted and the operating system loaded properly. To avoid future new arrests of the machine, the GPS has been removed. The shutter inside the monochromator had to be replaced due to a broken part. The new shutter was made with technical tips ensuring the correct operation for a long period of time. Next, a couple of Peltier cells for temperature control of the optical-mechanical unit has been replaced. To the optical unit no more operations were required. Substantial improvements were performed on Electronic Control Unit (ECU) to enable it to operate at low temperatures; a second ROI card (Relais Optocoupled port Interface) has been installed and an additional relais, for automatic control software from the cooling fans of the ECU has been setup. For temperatures greater than 25º the management software activates them until the set temperature is reached. The heat sink of the power MOSFET that regulates the voltage to the Peltier element for temperature control of the system was replaced with a more performant one. The entire electronic circuit of the ROI has been revised and a new layout was implemented that optimizes the operation of the Termoelectric cooler elements. A new algorithm was developed maintaining a temperature of /- 0.5º around the pre-set temperature. In order to monitor the temperature inside the PAT during the period of closure of the station, an external temperature sensor (AD590KH) connected temporarily to the input that was originally planned for the MIGE Alt -azimuth was added to the instrument. To bring into the ECU the temperature signal the parallel port connector (DSUB25) was used and the connections to the TAD (Temperature Adapter Device) have been modified.

The management software tool (DAS - Data Acquisition System) was upgraded and new features required by hardware changes were introduced. The activities at the University of Evora, were focused on the use of new electronic devices, namely the new AMS3-stepper motor controller - and the SESTILIO - a smart AD converter, that will be used for the upgrade of the instrument used in Antartica in the future expeditions. The work was developed mainly by the fellowship holder Rui Brito Mendes and new applications using the Qt framework were implemented and tested. The scientific line of research was mainly devoted to the processing and analysis of the data obtained from the SPATRAM/MZS and from the old GASCOD system. In addition, further research on methods and inversion techniques for the retrieval of NO2 and O3 vertical distribution were performed.

The fourth and last year of the MATAGRO allowed for one more expedition at the MZS station, where the ordinary maintenance of the spectrometric instrumentation was done:

The old GASCOD system was found in good condition even if the temperature inside the protective carter of the instrument was superior to 30º, for the failure of the fans that guarantee the ventilation inside the shelter. Both fans were replaced with equivalent devices. The normal cleaning of the parts of the optical and mechanical and optical fireplace for the entrance of the radiation was performed. The deep analysis of the management electronics contained in the carter containing the optical part had also highlighted the correct functioning of the whole system and no extraordinary operations on electronics or on program management tool was required. For the period from February to October 2014, the Gascod Control Box (GCB - installed in 2011) has correctly saved the data received by the control of GASCOD and has carried out the regular flow of information. The analysis of log files, revealed that no crashes occurred to the acquisition program

For the second year, the SPATRAM/MZS (Figure 3) has been operating successfully for the entire southern hemisphere autumn period. At the beginning of July, thanks to periodic inspections from Portugal by using the VPN connection Satellite, highlighted a malfunction probably due to a bug in the software that caused instability in the instrument performance. The problem was solved 'on-line'

Figure 3 - SPATRAM MZS-installed in working configuration inside the shelter called PAT.

The analysis of the conditions of the optical unit confirmed the goodness of the technical solutions adopted. The shutter replaced during the previous campaign was in perfect condition confirming that this shutter was made with technical solutions that guarantee the correct operation for a long period of time. The installation of the MIGE (Multi Input Geometry Device) required the intervention of logistics personnel, since it and was necessary to make 2 holes of 40 mm each in the roof of the shelter in order to allow the

passage of the optical fiber and the power cord of the platform to the central body of the spectrometer Furthermore, the logistics personnel has realized a support sealed in steel, to support the device and fix it rigidly to the container roof. The installation required a considerable work of adaptation of the internal connections of the MIGE device The final setup is shown in Figure 4.

Figure 4 – on the left the VELOD (Vertical looking Device - operational since February 2013) and on the right the alt azimuth platform called MIGE (Multiple Input Geometry Equipment - setup in November 2014). Both systems are connected to the spectrometer via fiber optics.

The acquisition software -DAS- has undergone some changes to allow the use of the platform. Furthermore new pre-defined measurement cycles, contained in the file that the DAS interprets to perform the measurements. Particular attention was then used in the modification of the algorithm used for temperature control: the thermal inertia of the instrument is very high, so it is quite difficult to reach a stable thermal equilibrium, also because the Peltier system provides both heating and cooling as possible options. Upon reaching the operating temperature from a temperature higher, the inertia of the instrument would lead to activate the heating and vice versa. The strict application to the thermoregulation procedure of the exactly calculated PID (Proportional Integral Derivative) parameters, would cause the continuous action of the relays determining the direction of the TEC (Thermo Electric Cooler) current. Therefore, it was chosen to underestimate the parameter that constitutes the constant of proportionality of the PID obtaining a deviation of 0.5ºC on the set temperature, but with an accuracy of +/- 0.2ºC.

The spectral data collected during the period of operation of instruments (GASCOD and SPATRAM/MZS) were partially analyzed in accordance with the algorithms of the differential optical absorption

spectroscopy (DOAS) to check for any problems that occurred during the period. The results obtained with the GASCOD have revealed the expected seasonal variation of columnar content of NO2 (Figure 5).

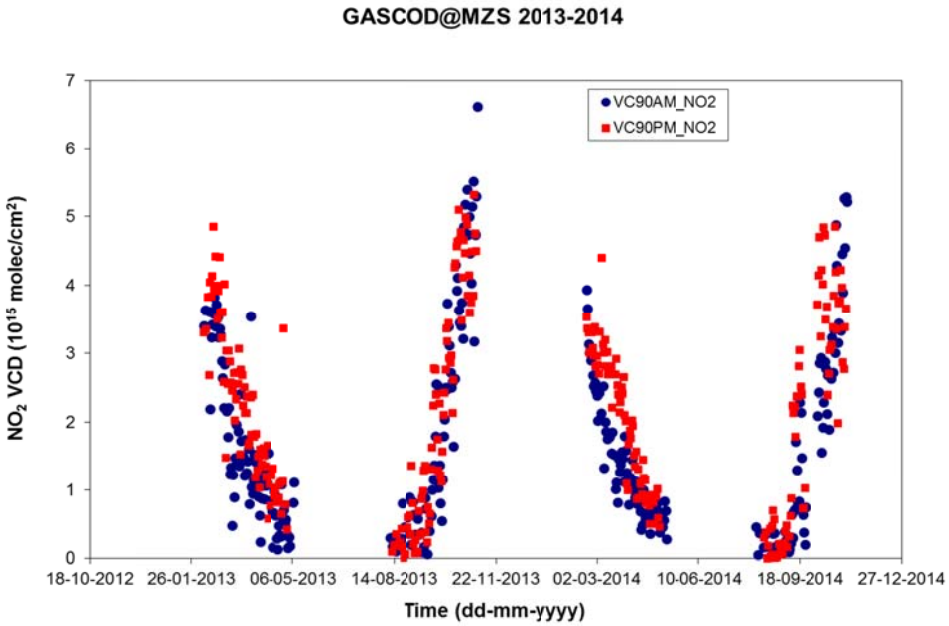

Figure 5 – NO2 Vertical columns for the years 2013-2014

The data analysis of spectral raw data measured with the SPATRAM/MZS allowed to obtain for the first time at the MZS station, the diurnal variation of O3 and ClO2 in a spectral range never observed before with the old GASCOD spectrometer (Figure 6).

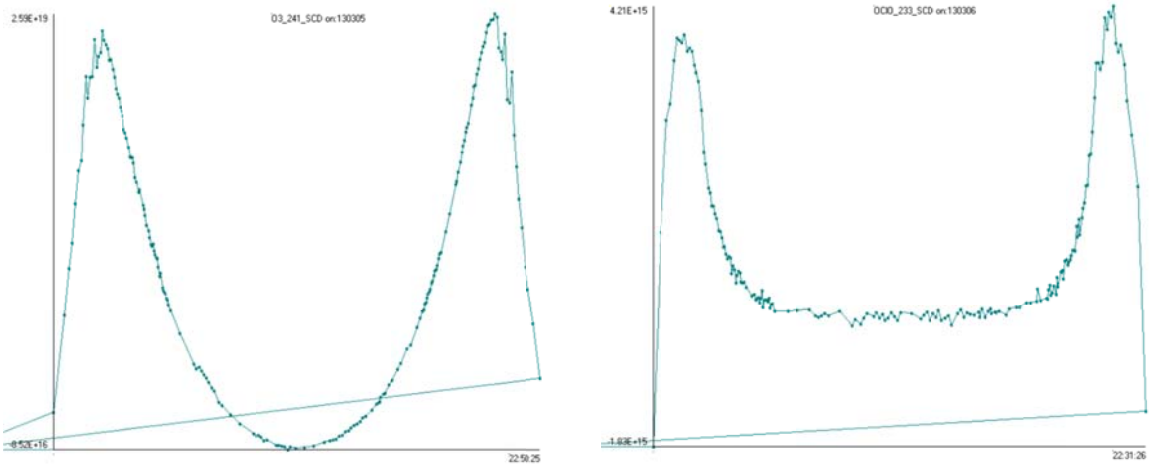

Figure 6 – Diurnal variation for O3 (left panel) and ClO2 (right panel) observed during the beginning of March 2013 with the SPATRAM/MZS

The above described activities deal mainly with the work on field carried out during the last 4 years in the Antarctic region. The scientific outcomes of these project are not described deeply here since all the informations are contained in the more than 20 publications involving the MATAGRO project and listed in the indicator table part of this report.

The research is only at the beginning, since data are not still completely processed and analyzed. In addition after this experience, the field of investigation is wider than before since we would like to add other capabilities of measurements to the hardware now installed in Antarctica as described in the MATAGRO2 research project recently submitted to the FCT for evaluation.

Furthermore, the University of Evora, will host the Portuguese Conference on Polar Research that will take place the 27-28 October 2015 in Evora, where the portuguese Polar community will present results from the last measurement campaign in Arctic as well as in Antarctic regions.

Last but not least, MATAGRO allowed for the formation of two young researchers (Hermano Tiago Martins and Rui Brito Mendes – this last accomplished the Master degree at the University of Evora) in polar atmospheric science.