Ground-based and satellite measurements of stratospheric nitrogen dioxide and ozone over the south of Italy

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Abstract —
Nitrogen oxides as well as ozone play a central role in atmospheric chemistry and the improvement of techniques and instruments allowing for a better understanding of the distributions and behaviour of the mentioned compounds are strongly required by the scientific community. Thanks to the new satellite technology, global scenes of the dynamical and chemical processes of the atmospheric compounds can be drawn. Ground-based equipments have to be used for comparison/validation of the satellite retrievals. The LIS (Lampedusa Island Spectrometer) instrument is a SPATRAM (SPectrometer for Atmospheric TRacers and Aerosol Measurement) type equipment allowing for the measurements of spectral sky radiance along the zenith direction, in its standard configuration. Here, the first results obtained with the LIS spectrometer installed in the centre of Palermo (Italy) for nitrogen dioxide (NO_2) and ozone (O_3) total columns, and the comparisons with data from the OMI – Ozone Monitoring Instrument on board of AURA satellite for O_3 total column are presented and discussed.

Keywords — nitrogen dioxide, ozone, remote sensing, spectrometer

1 INTRODUCTION

In the last thirty years, the stratospheric ozone in the Northern Hemisphere (NH) mid-latitudes has suffered a meaningful decrease. The analysis of results obtained from TOMS (Total Ozone Mapping Spectrometer), installed on the Nimbus 7 satellite, underlines the significant reduction of the ozone total column also before the Pinatubo eruption. During the eighties, studies on ozone profile temporal series in the NH show that the annual average ozone concentration increases in troposphere and decreases in the low stratosphere [1]. Other authors confirm these results [2, 3], underlining that in Southern Europe, the values of the stratospheric ozone trend per decade are higher than those found in the United States, also considering areas at the same latitudes and with equal values of superficial nitrogen oxides. Comparisons of the results obtained for both hemispheres lead to the conclusion that ozone loss is smaller at northern high latitudes than the Antarctic depletion phenomena. At mid-latitudes this difference is balanced with equivalent values between 5% and 8% per decade [4], but it would seem greater in the NH. Nevertheless, the physical processes that can justify these losses in the ozone budget of the north mid-latitude, is not completely explained. The hypothesis of the air masses transport from the polar vortex towards the South Hemisphere (SH) cannot be completely applied for the NH. In fact, Arctic regions show very different meteorological conditions as higher average temperatures that do not favour the Polar Stratospheric Clouds (PSCs) formation. On the other hand, the lower polar vortex strength allows for losing its shape causing air masses intrusions until the mid-latitudes.

For some years the nitrogen compounds were thought to be the greatest responsible for the ozone catalytic destruction. The understanding of the dynamical processes, chemical and photochemical reactions involving nitrogen compounds in the stratosphere has improved. The existence of a winter drop in NO_2 total column at high latitudes has been explained by the coupling of dynamical and chemical phenomena [5]. As clearly shown by

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Noxon [6], the horizontal transport plays a very important role at mid-latitudes: air can move very rapidly from the high to the low latitudes, depending on the weather conditions. Sometimes this process of dislocation is slow so the chemistry of NO, NO_2, N_2O_5 and HNO_3 can play the primary role in the nitrogen compounds partitioning, that follow the change in temperature and in insolation time caused by the slow air movement. Besides, now we know more about the interference between ClOx and NOx family cycle. Chlorine nitrate ($ClONO_2$) is formed by the NO_2 that reacts with ClO, giving a long-lived reservoir, thus inhibiting the large catalytic ozone depletion potential of the chlorine monoxide as hypothesized by [7].

In this context, the LIS (Lampedusa Island Spectrometer) instrument, originally developed for the Lampedusa climatic station [8], is now installed in the centre of Palermo (38.13°N, 13.35°E) at the Unit for Environment and Energy Modeling (UTMEA) of the Italian National Agency for new technology (ENEA). LIS carrys out automatically regular measurements of zenith sky scattered radiation. The lack of atmospheric chemistry measurements in the South of Italy, together with the fact that this is one of the regions of the European countries with the highest insolation, constitutes the key motivations for the measurements presented in this work.

This study presents trace gases vertical column results obtained from DOAS (Differential Optical Absorption Spectroscopy) methodology applied to the first data of diffused zenith sky radiation obtained with the LIS instrument, In addition, the comparison with equivalent results obtained from the OMI satellite borne equipment is presented and discussed.

2 INSTRUMENTAL SETUP AND METHOD

The LIS is a UV-Vis spectrometer for the measurements of the solar scattered radiation along different directions. The instrument was developed by the Atmospheric physics group of the University of Evora (UE) thanks to a collaboration with the ISAC-CNR Institute in Italy and with the initial support of the Italian National Agency for new technology (ENEA). LIS is installed since September 2010 in the Observatory of the Unit for Environment and Energy Modeling (UTMEA) Centre (Fig. 1) in Palermo. LIS instrument belongs to the SPATRAM family [9] and here only the main features of the instrument are highlighted

The spectrometer is installed inside a thermostatic box able to keep the internal temperature within the working range of the instrument (typically 20°C for the Optical Unit).

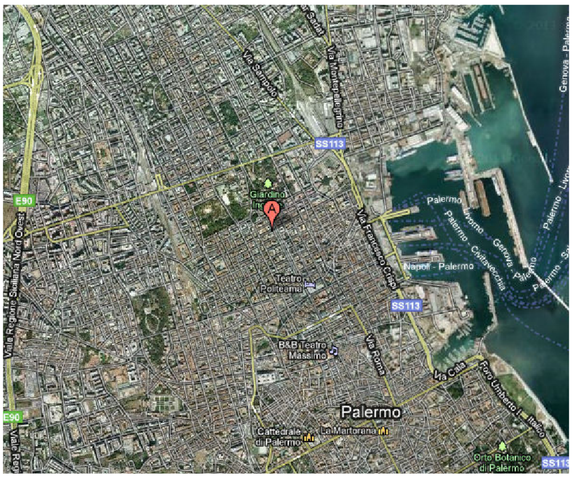

Fig. 1. Location of the LIS spectrometer in the Centre of Palermo - Italy

The equipment (shown in Fig. 2) allows for multiple input of the radiation: from the primary input that is composed of a series flat and spherical mirror that focalize the light beam on the entrance slit (0.1 x 8 mm); from the optic fibre inputs where the signal is carried to the entrance slit with an optic fibre linked to a optic system. A rotating mirror, driven by a stepper motor, allows for choosing between the primary input. the optic fibre ones and the additional input for spectral or radiometric calibration.

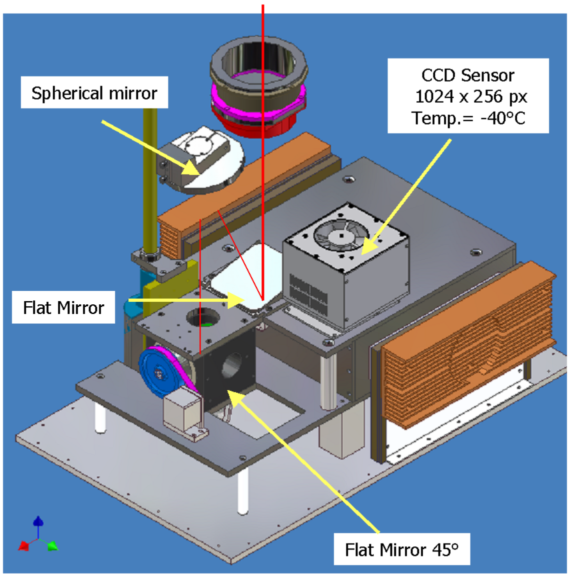

Fig. 2. Schematic view of the Optical Mechanical Unit (OMU) of the LIS equipment

The spectrometer is composed of a holographic spherical diffraction grating of 1200 grooves/mm and a Back Illuminated CCD sensor array by e2v technologies customized for ours scopes by DTA (www.dta.it). The spectral dispersion is approximately 2.4 nm/mm (depending on the investigated spectral region), and the overall typical spectral resolution is about 0.5 nm. The grating is controlled by a stepper motor which, by varying the angle of incidence of light, allows the instrument to obtain measurements from 250 to 950 nm. in spectral windows of 60 nm each. For atmospheric measurements the spectral range 300-600nm is usually used. The CCD camera has a big quantum efficiency allowing to perform the so-called 'vertical binning' of the vertical pixels in order to obtain an higher signal to noise ratio. In order to minimize the effects of the dark and read current one double stadium Peltier circuit cools the CCD chip till –40°C. Band-pass filters are used to reduce the stray light inside the spectrometer and neutral densities filters are adopted to prevent the CCD saturation with high radiation fluxes. The integration time is automatically selected for each reading and ranges from tenths of milliseconds at noon to a tenth of seconds at twilight. An internal mercury lamp is used for periodic checks of the diffraction grating positions, ensuring a spectral accuracy of better than 0.2 nm.

The Electronic Control Unit (ECU) is equipped with 1GHz CPU. The SPATRAM is handled by a software tool (DAS – Data Acquisition System) that was developed in order to manage all the spectrometer devices and for automatic scheduled measurements and unattended mode as per predefined measurements cycle; the ECU provides also to the storage of the recorded spectra and to their first analysis, with DOAS methodology, in order to obtain the vertical content of the species presenting absorptions features in the selected spectral range.

The OMI satellite instrument is a contribution of the Netherlands's Agency for Aerospace Programs (NIVR) in collaboration with the Finnish Meteorological Institute (FMI) to the NASA EOS-Aura satellite platform launched in July 2004 [10]. OMI currently continues the global total ozone column measurements recorded by the NASA Total Ozone Mapping Spectrometer (TOMS) instruments since 1978. The OMI instrument is a nadir viewing wide swath UV-VIS hyperspectral spectrometer measuring solar light reflected and backscattered from the Earth's atmosphere and surface in the wavelength range from 270 nm to 500 nm with a spectral resolution of 0.45 nm in the ultraviolet and 0.63 nm in the visible. The instrument has a 2600 km wide viewing swath such that is capable of daily, global contiguous mapping of total ozone with an unprecedented high spatial resolution of 13x24 km^2 at nadir. The OMI total ozone column data used in this work were obtained from the OMI-DOAS algorithm [11] developed at Royal Dutch Meteorological Institute (KNMI) which is based on the DOAS technique.

The full explanation of the DOAS technique is beyond the scope of this work and can be found in references [12, 13]. Nonetheless, a brief summary of the main DOAS algorithms is provided here. The absorption structure of the gases under investigation, are obtained removing the Fraunhofer lines of the solar spectra. The logarithm of the ratio (Log-Ratio) between the reference spectrum (Io) and the twilight spectrum (Is) is calculated. Applying a Low Pass Filter operator (LPF(x)) to the Log-Ratio spectrum, the high frequency features of the spectral series are removed. The 'differential' spectrum - the difference between Log-Ratio and LPF(Log-Ratio) - is compared with the Differential absorption Cross Sections (DCS) of the gases under investigation, presenting marked absorption features in the selected spectral range. Since the reference spectrum is measured at the local noon, when the absorption of the minor compounds is negligible but not zero, the retrieved values for the investigated species are the Differential Slant Column Density (DSCD). The DSCD are the differences between the gas content in the analyzed spectrum and the reference one. Aiming to obtain values of Slant Column Density (SCD), the problem of the absorber content in the reference spectrum, arises. At mid-latitudes usually the Langley plot of the AM and PM measurements versus the series of the Air Mass Factors, is utilized for the calculation of the minor compounds content in the reference spectrum. For Polar Regions the problem is solved with some simple considerations based on the chemical equilibrium reached during the 24h polar day periods [14].

4 RESULTS AND DISCUSSION

Before processing the data with DOAS methodology, the ratio between the signal obtained by the spectrometer during each measurement and its "exposure" time is calculated in order to obtain information on the performance of the instrument and the quality of the data obtained. This ratio is called the 'Flux Index' (FI). It provides data on the variation of the incoming radiation quantity. Figure 3 shows the FI for 5 days under different meteorological conditions at Palermo station. During cloud-free days the FI values describe a regular function. In cloudy conditions, the data are more scattered mainly due to the increase in the forward scattering caused by the marked phase function asymmetry of the diffusing particles However, the measurements obtained with the LIS spectrometer are not affected by the change in radiation flux, since the raw data are carried out by applying the 'auto ranging mode' in order to find the optimal integration time and, hence, achieve a high S/N ratio.

In order to obtain the differential slant column density (DSCD) of the investigated species, the DOAS algorithms are applied in the 425-455 nm and 320-340 nm spectral windows, where the strongest absorbers are NO_2 and O_3, respectively.

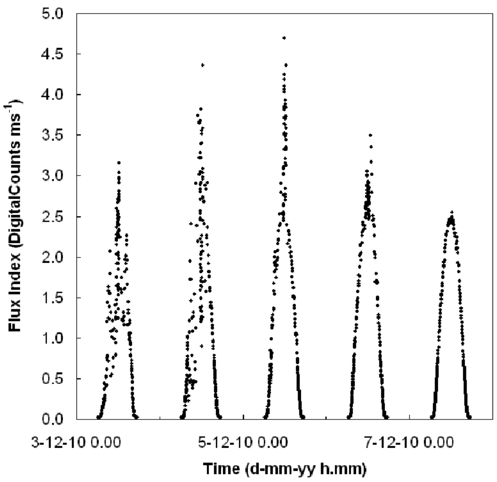

Fig. 3. The Flux Index calculated for 5 days of LIS measurements in Palermo.

The vertical column densities (VCD) of the investigated compounds are obtained applying the air-mass factor (AMF) calculated with the AMEFCO RT model, to the SCD. In order to avoid bias due to the seasonal dependency of the vertical profile and hence in the AMF, different boundary condition are applied to the model with the aim to distinguish summertime and wintertime air masses. Since the SPATRAM does not perform measurements at a fixed value of Solar Zenith Angle (SZA), the value at a given SZA (90° for NO_2 and 87° for O_3) is calculated with a cubic interpolation of the data. The errors associated to the presented results are in the range of 3-5% for the VCD at 90° and of 2-3% for the VCD at 87°. Values with larger errors, due to very low signal intensity, are rejected.

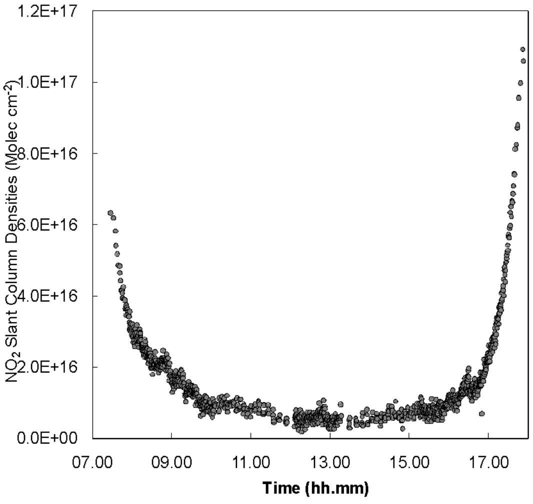

Fig. 4. The NO_2 Slant column densities (SDC) daily variation during 21 January 2011 retrieved from the LIS spectral measurements.

Figure 4 shows the NO_2 SCDs plotted versus time, for 21 January 2011. To note that the maximum sunrise values (AM) and sunset values (PM) values are of $(6.34 \pm 0.06)\times10^{16}$ and $(10.92 \pm 0.09)\times10^{16}$ molecules•cm^{-2}, respectively. The graph reveals the tendency for the increase of NO_2 SCD, during the day, especially from early in the morning till around 11:00 UTC and then from 14:00 to 18:00 UTC. The tendency for the increase is less evident around midday, which is due to the fact that the measurement errors increase when more direct solar radiation enters the instrument and influences the spectral measurements, increasing the noise (decreasing the signal-to-noise ratio - SNR). This reflects in higher errors in the slant column retrievals. On the other hand, the fact that the AMEFCO, used to calculate the air mass factor, is not a photochemical but a probabilistic model, causes an amplification of the errors when the VCD is calculated.

The photochemical activity of the NO_2 is the main reason for the typical diurnal variation of the SCD with the PM values, systematically higher than the AM values. NO_2 can be oxidized by O_3 to form NO_3, a strong atmospheric oxidant and a precursor to the formation of dinitrogen pentoxide, N_2O_5. Because NO_3 is rapidly photolyzed at visible wavelengths, both its daytime concentration and chemistry are of relatively minor importance in the lower and middle stratosphere. In contrast, N_2O_5 can have morning concentrations in the lower stratosphere comparable to NO_x (NO+NO_2) even though its production requires the formation of NO_3.

The explanation results primarily from the different photolysis rates of N_2O_5 and NO_3. During the night, N_2O_5 is formed at the expense of NO, or more precisely at the expense of NO_2. After sunrise, N_2O_5 can be photolyzed essentially into two NOx molecules. The photolysis time depends on factors like the solar zenith angle, the altitude, the albedo and the temperature.

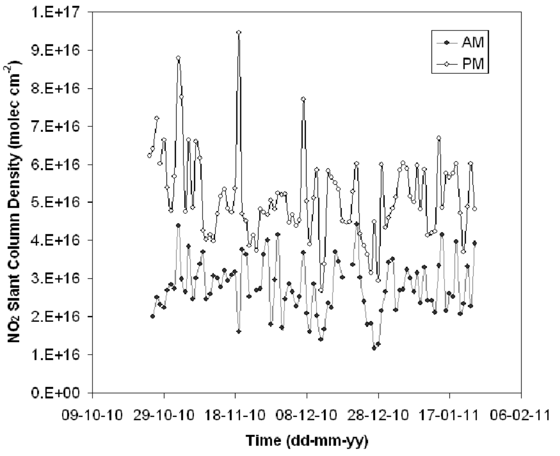

Fig. 5. The NO_2 Slant Column Densities at 90° of Solar Zenith Angle during sunrise (AM) and sunset (PM) for the period November 2010 - January 2011 in Palermo.

The above discussion is exemplified in Figure 5, where the NO_2 SCD values obtained for the sunrise period (at 90°of Solar Zenith Angle) are systematically lower than the ones calculated for the sunset times.

The O_3 photochemical activity is not so pronounced as for NO_2; actually the plot in figure 6 confirms that the AM and PM values are essentially the same.

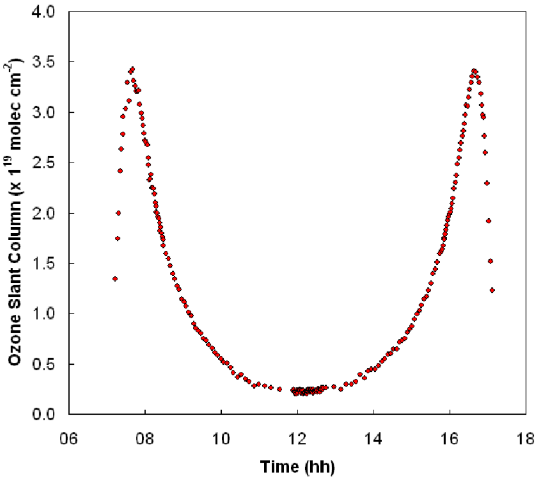

Fig. 6. The O_3 Slant Column Densities daily variation for the 29 December 2010 as measured with LIS in Palermo.

One more evidence can be found in figure 7, where the O_3 SCD values are plotted versus the SZA in order to examine the different behavior, in terms of photochemical activity and diurnal variation, of O_3 respect NO_2. Whereas the maximum values of NO_2 SCD are obtained for the uppermost SZA (93°), for O_3 the upper limit of (3.51 ± 0.04) × 10+19 molecules cm^{-2} for SZA of 87° is measured

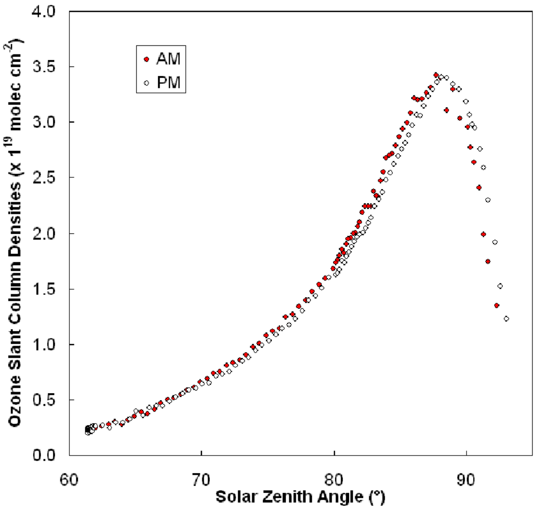

Fig. 7. The same of Fig.6, but the O_3 daily variation is function of the Solar Zenith Angle.

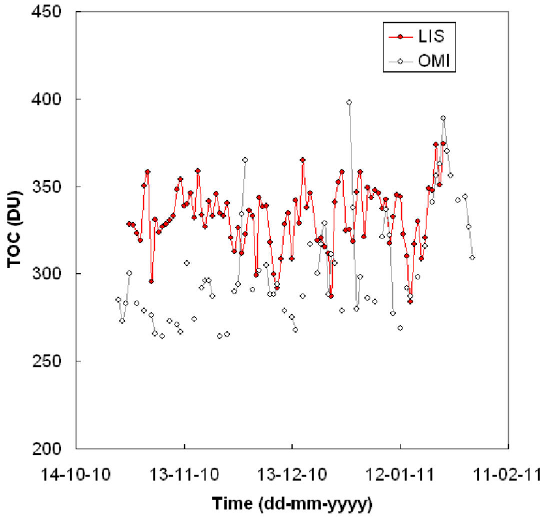

Fig. 8. The Total Ozone Column (TOC) time series (red circles) for the full period of the analyzed LIS measurements in Palermo together with the OMI data (white cicles).

The comparison of the O_3 results obtained with the LIS instrument with other satellite borne equipment are showed in figure 8. In this plot the LIS results for Ozone VCD are the daily averages of all the data obtained during the period of activity of the instrument during the day (for SZA in the range 65°-95°, in order to maximize the signal to noise ratio of the measurements)

The OMI results are in good agreement with the SPATRAM data. The episodically events of under or over estimation of the ozone VCD of the ground based equipment are mainly due to the different meteorological conditions of the zenith sky measurements and to the point of view of the instruments (from the space and from the ground).

8 CONCLUSIONS

The goal to install an automatic DOAS instrument at the Observatory of Palermo for the measurements of atmospheric tracers in unattended mode was reached. Vertical columns of NO_2 and O_3 for the first 60 days of measurements are presented and discussed. The seasonal trend and the diurnal variations for the column values of NO_2 show a good agreement with both the photochemical theory of the NO_x family and values observed by other authors in mid-latitude sites and with similar instrumentation [15, 16]. Observation of nitrogen dioxide can improve our understanding of the complex physical and chemical processes in the stratosphere.

No evident problems occur to the optical equipment during the period of activity.

The comparison of the LIS results with satellite borne equipment shows a good agreement, encouraging the possibility to continue with the work of validation of the satellite results. This activity could be enlarged as the LIS is similar to other spectrometers installed at the Ottavio Vittori Station in Mt Cimone (Italy), at the Bulgarian Atmospheric Station in Stara Zagora, at the Observatory of the Geophysics Centre of Evora (Portugal), at the Mario Zucchelli Italian Antarctic Station, and in a near future in the Indian Antarctic Station of Maitri.

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