



Determination of the seasonal variation of the nitrogen dioxide and ozone vertical column density at Río Gallegos, Santa Cruz province, Argentina, using a zenith-sky DOAS system

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SUMMARY

Stratospheric ozone (O_3) plays a critical role in the atmosphere by absorbing most of the biologically damaging solar UV radiation before it reaches the Earth's surface. Nitrogen dioxide (NO_2) is a key trace gas in the ozone photochemical. The systematic sensing of NO_2 and other minority gases is essential in order to understand the stratospheric O_3 destruction and formation processes. We present the study carried out on the seasonal variation of the O_3 and NO_2 vertical column density (VCD), using a zenith-sky DOAS (Differential Optical Absorption Spectroscopy). This system is composed of a spectral analyzer (portable spectrometer HR4000, Ocean Optics), two optical fibers (400 μm of core, 25 cm and 6 m of longitude) and an automatic mechanical shutter. NO_2 and O_3 VCD are derived from solar spectra acquired during twilights ($87^\circ - 91^\circ$ zenithal angles). The data retrieved by our instrument are compared with those coming from the SAOZ spectrometer (Système d'Analyse par Observation Zenithale, Laboratoire Atmosphères, Milieux, Observations Spatiales (LATMOS), France). Both systems are located in Rio Gallegos, Santa Cruz province, Argentine ($51^\circ 36' S$; $69^\circ 19' W$, 15 m asl), in the CEILAP-RG remote sensing station.

Key words: zenith-sky DOAS, NO_2 , O_3 , OMI, SAOZ

INTRODUCTION

Stratospheric ozone (O_3) plays a critical role in the atmosphere by absorbing most of the biologically damaging solar UV radiation before it reaches the Earth's surface. The most important nitrogen species emitted to the atmosphere are nitrous oxide (N_2O), nitrogen oxides ($NO_x = NO + NO_2$) and ammonium (NH_3). N_2O is an important greenhouse gas which is naturally emitted by earth and sea bacteria, and also produced by human activities, mainly agriculture. It is a very stable molecule which is transported to the stratosphere. In the middle and upper stratosphere N_2O is converted to NO by reaction with excited oxygen atoms O (1D) produced mainly by UV photolysis of O_3 (Fish and Jones, 1995).

During daylight a balance between NO and NO_2 concentrations is established through the reaction of the former with O_3 and the rapid photolysis and reaction with atomic oxygen of the latter. At night, NO_2 is converted first to NO_3 and via a three-body reaction to the N_2O_5 reservoir. This causes a build-up of N_2O_5 during the night followed by a slow release during the following day through photolysis. The diurnal variation of NO_2 therefore comprises a maximum immediately after sunset, followed by a slow decrease throughout the night and a sharp drop to minimum at sunrise.

As well as the diurnal variation there is a seasonal variation in stratospheric NO_2 at mid-latitudes due to the combined effects of photochemistry and atmospheric transport (Gil et al., 2007).

The development of remote sensing systems for monitoring of trace gases is fundamental to understand the dynamic processes that occur in the stratosphere. The LIDAR Division (CEILAP-CITEDEF) has in Río Gallegos, Santa Cruz province ($51^\circ 36' S$; $69^\circ 19' W$; 15 m asl) a remote sensing station (CEILAP-RG) where systematically are carry out measurements of several atmospheric parameter (www.division-lidar.com.ar), as for example: the concentration in vertical column O_3 and of NO_2 , the O_3 concentration discriminated in height (O_3 profile obtained by LIDAR, between 15 and 45 km), aerosol optical thickness, solar irradiance (UV-A, UV-B, NIR), etc. It is necessary to highlight that Río Gallegos city is affected every spring by a significant decrease of the stratospheric O_3 that produces an increment of the UV solar radiations that arrive to the surface.

MATERIALS AND METHOD

We present the development of a compact atmospheric remote sensing system, able to determine the VCD (Vertical Column

Density) of multiple trace gases. It is a low-cost and portable zenith-sky DOAS system (Figure 1) - hereafter referred to as ERO-DOAS - composed of a mini-spectrometer (HR4000, Ocean Optics), two optical fibers (400 μm of core, 6 m and 25 cm of longitude) and a home-made external shutter (Raponi et al., 2011).

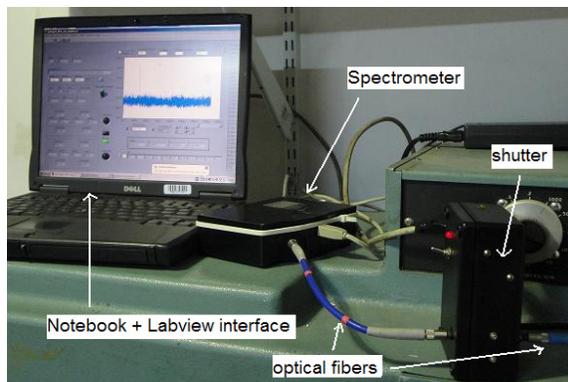


Figure 1. The zenith-sky DOAS system's components: a notebook, the software designed using Labview®, the spectrometer (HR4000), an automatic shutter and the optical fibers.

HR4000 allow us to measure solar spectral irradiance in the UV-visible range (290-650 nm). It is a simple spectrograph equipped with a fixed diffraction grating (600 grooves/mm blazed at 400 nm) and a 3648-pixel linear array CCD. We developed an automatic shutter to determine the dark current of each measurement, and to remove this noise to the twilight spectra. A software development using Labview® controls the start and the end of spectral measurements, the retrieval of acquired spectra and the shutter. The computer internal clock is daily updated to avoid possible time shifts and to maintain accuracy on zenithal and azimuth angles calculations.

The software sets the CCD integration time to maximize signal/noise ratio. The dark (current) spectra are measured with the same integration time than the twilight spectra measured immediately before. This ensures that the subtracted dark noise is similar to the one actually measured over the illuminated period.

The instrumental function and the system resolution were determined using low pressure lamps spectra provided by the Physics Laboratory of Instituto Tecnológico de Buenos Aires (ITBA). We retrieved the spectrometer instrument function from a helium lamp. The full width at half maximum (FWHM) of the Voigt profile fitted to the He line was 1.03 nm at ~ 447 nm. The lamp spectra were also used to recalibrate ERO's wavelength mapping. This recalibration shows a shift of about -1.55 nm from the original (nominal) manufacturer calibration.

The analysis of visible spectra based on the DOAS concept presents the advantage of allowing for simultaneous retrieval of VCDs of different species, over a wide range of meteorological conditions. NO₂ and O₃ VCDs are retrieved from zenithal solar spectra (in the visible range) acquired on "twilight" conditions (zenithal angle between 87° and 91°) applying the DOAS (Differential Optical Absorption Spectroscopy) technique.

RESULTS

We present a study on the O₃ and NO₂ VCDs seasonal variation at Río Gallegos. In Figure 2 we can observe the NO₂ VCD seasonal variation at Río Gallegos during 2004-2011, retrieved by OMI/AURA. The concentration ranging from 6×10^{15} molec/cm² in summer to 1.6×10^{15} molec/cm² in winter and early spring.

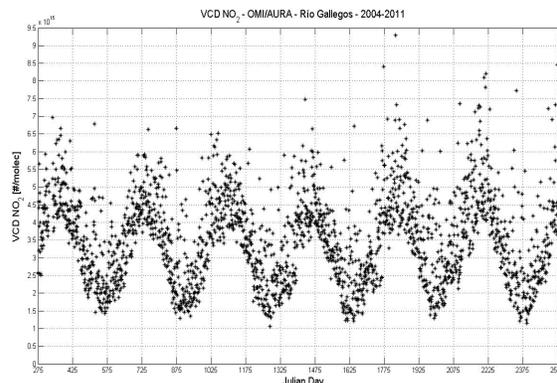


Figure 2. NO₂ VCD variability at Río Gallegos, Santa Cruz province, Argentina, retrieved by OMI-AURA, from 2004 to 2011.

Figure 3 show the NO₂ and O₃ vertical column densities obtained with a SAOZ spectrometer (Système d'Analyse par Observation Zenithale), LATMOS (Laboratoire Atmosphères, Milieux, Observations Spatiales), France, located in the CEILAP-RG station, during 2009.

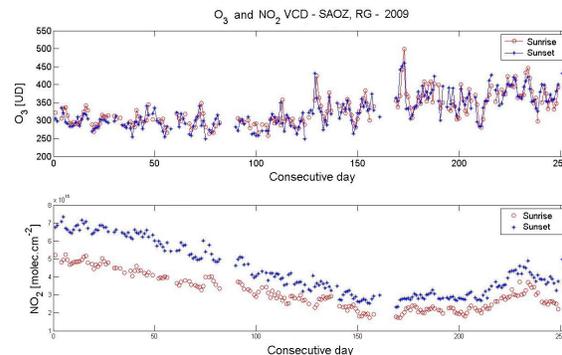


Figure 3: NO₂ and O₃ VCD seasonal variation during 2009, retrieved by SAOZ spectrometer at Río Gallegos.

In the case of the O₃ VCD significant differences are not observed among the concentrations at sunrise and at sunset, as we waited. In the case of NO₂, to be a gas with a comparatively short photochemical time of life, it presents a significant variability during the day. For that reason, an important difference among the concentrations measured during the twilights, exist.

In Figure 4 we compare the O₃ and NO₂ VCD retrieved by ERO-DOAS and SAOZ spectrometer (both of them located in CEILAP-RG station), during September/December 2009.

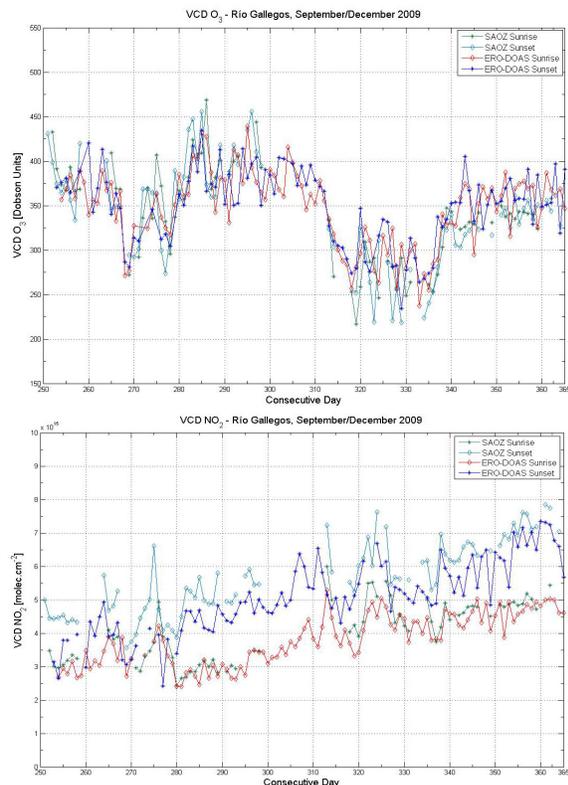


Figure 4. O₃ and NO₂ VCD retrieved by ERO-DOAS and SAOZ instruments at Río Gallegos, during September/December 2009.

For the ozone there is a good agreement among the instruments with an average relative difference about 13%. In the case of NO₂, we observe a better agreement among results at sunrise than at sunset between SAOZ and ERO-DOAS data.

CONCLUSIONS

Our zenith-sky DOAS system has the capability of sensing automatically several chemical species and the advantage of being portable (which offers the possibility to move the instrument to carry out measurements campaigns). We observe in both ground-based instruments a strong daily variability of the NO₂ VCD (sunrise vs. sunset). This variability is probably associated with the NO_x vertical distribution, the temperature in the high layers of the atmosphere and maybe the variability of other active species. In the case of the O₃ the daily variability of the gas is low, reason why the comparison between the sunrise and sunset data is very good.

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REFERENCES

- Fish, D., and R. Jones (1995), Rotational Raman scattering and ring effect in zenith sky spectra, *Geophys. Res. Lett.*, 22 (7), 811-14.
- Gil, M., M. Yela, L. Gunn, A. Richter, I. Alonso, M. Chipperfield, E. Cuevas, J. Iglesias, M. Navarro, O. Puentedura and S. Rodriguez (2007), NO₂ climatology in the northern subtropical region: diurnal, seasonal and interannual variability, *Atmos. Chem. Phys. Discuss.* 7, 15067-103.
- Raponi M., R. Jiménez, E. Wolfram, J. Tocho, E. Quel (2011), Remote sensing of stratospheric NO₂ over the Argentinean Antarctica using a DOAS mini-spectrometer, *Óptica Pura y Aplicada*, 44 (1), 77-82.