NO_2 AND SO_2 CONCENTRATION TROPOSPHERIC PROFILES IN THE LAGOON ENVIRONMENT OF VENICE

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ABSTRACT

An optimal estimation based inverse method, used to retrieve the vertical profiles of a specific trace gas in the troposphere, is presented. The vertical distribution of trace gases, such as NO_2 and SO_2 has been retrieved by means of the spectral measurements performed with a spatial scanning DOAS system. The latter is composed of the UV-Vis spectrometer TROPOGAS (TROPOspheric Gas Analyser Spectrometer) coupled with an optical fibre to the scanning telescope SODCAL (Scanning Optical Device Collecting Atmospheric Light). The measurements have been carried out for the 2007, 2008 and 2009 summer periods, during field campaigns performed in the lagoon area of Venice, Italy. The spectra measured for various elevations of the SODCAL zenith axis, have been analysed according to the DOAS methodology, yielding the so-called Slant Column Density of the analysed atmospheric compounds. The application of the inversion method, together with the a-priori assumption and the radiative transfer calculations provides the tropospheric profiles. The results show high pollution levels in both the NO_2 and SO_2 concentration, probably due to the numerous sources in the neighbouring area such as the power plant, the harbour, the boat traffic, etc. The integrated tropospheric NO_2 column obtained from the gas profile has been compared with the simultaneous tropospheric column provided by the OMI satellite sensor. Discussions about the method, the retrieved results, the comparison with OMI data and the factors that could influence the previous items (e.g. cloud cover) are provided.

1. INTRODUCTION

DOAS (Differential Optical absorption spectroscopy) is a technique that identifies and quantifies trace gas abundances with narrow band absorption structures in the near UV and visible regions [1]. DOAS was first applied to zenith sky scattered radiation measurements. The radiation input of the measuring equipment (usually an UV-Vis. spectrometer) is pointed towards the zenith and the outputs of the DOAS processing are the Slant Column Densities (SCDs). The impossibility to define exactly the OMP (Optical Measurement Path) requires additional computations with a Radiative Transfer Model (RTM) in order to retrieve the 'geometrical factor', known as Air Mass Factor (AMF), for the 'correction' of the SCDs. The AMF allows for the determination of the Vertical Column Density (VCD) of the analysed atmospheric compound since AMF = SCD/VCD [1]. The results obtained with this type of measurements are often used in studies concerning modifications in the total content of atmospheric compounds, mainly located in the stratosphere. These works are mostly inserted in the frame of global warming and climate changes.

Recently, the DOAS observations are performed also for direction away from the zenith one (Off-Axis or Multi Axis mode). This method is particularly suitable for the monitoring of tropospheric compounds due to enhanced sensitivity of the off-axis technique [2] in the lower troposphere. The main problem in the interpretation of the measured SCD is related to the determination of the OMP, that has to be calculated accounting for the multiple scattering, since this last has an increased weight on the Off-Axis measurements. The researches related to the Off-Axis results, mainly due to their tropospheric feature, are inserted in the framework of the air quality and environmental investigations.

Actually there are different algorithms to retrieve gas [2] and aerosol [3, 4] profiles applicable to DOAS measurements; most of them focused on the minimization of the residual of the difference between an a-priori guess profile and the retrieved one.

In this framework, the optimal estimation method is one of the most used, and here is applied to retrieve vertical profiles distribution of NO_2 and SO_2 inside the first km of troposphere. In addition, the NO_2 tropospheric vertical columns are calculated from the ground based observations and they are then compared with the tropospheric values obtained from the OMI satellite sensor (www.TEMIS.nl). The discussion about the factors influencing the accuracy of the method is also provided.

2. SITE DESCRIPTION AND METHOD

Measurements are performed during the summer periods: 28/06 - 24/07/2007, 23/09 - 27/10/2008 and 21/07 - 23/10 2009, in Venice, Italy (45° 26' N, 12° 20') with a scanning DOAS system [6]. The latter is composed by an UV-Vis spectrometer TROPOGAS (TROPOspheric Gas Analyser Spectrometer) coupled by optical fibre to a rotating telescope SODCAL (Scanning Optical Device Collecting Atmospheric Light). Venice is a particular city because the main citizen transport is represented by boats, with diesel engine. For this reason high SO_2 concentrations are expected. The spectrometer was used in the MAX-DOAS [4] configuration, locking at the a = 1°, 2°, 4°, 8°, 16°, 30°, 32° angle of sight [7]. In Fig. 1 is represented the Venice lagoon, with a black "X" which denotes the position of the TROPOGAS spectrometer and with a black line that show the azimuth of measurements.

Figure 1. Venice and its lagoon environment. The black "X" shows the instrument position while the black line shows the line of sight direction.

The vertical distribution retrieval is based on the Optimal Estimation Method [8]. Given an atmospheric state **x**, a forward model F, typically represented by a Radiative Transfer model, can simulate the measurement process **y**=F(**x**). The vector **y** is composed by all measured SCDs obtained at different angles of sight $a_1, \dots, a_n$, and the state **x** is composed by the trace gas concentrations vertical profiles $C(h_1, \dots, h_n)$. The inverse model is a typical ill-posed problem with no unique solution. This means that all possible states that are consistent with the measured information can be found in the atmosphere. However, the probability density functions of each state can be calculated if the following information are provided: (a) any *a priori* information about the unknown state; (b) a measurement together with a description of its error statistics and (c) a forward model. This permits to get the optimal estimation solution of the atmospheric state vector **x**, according to the measurement vector **y**, the atmospheric model F and the model and measurement statistic. The MOCRA (MOnte Carlo Radiance Analysis) model is used in this works [9]; it provides the box AMF_i that represent the inverse model of the simulated measurements. The box AMF_i applied to measurements vector produces the atmospheric vertical profiles. At this point any information about the state vector can be used to calculate the best solution. An iterative algorithm based on the Levenberg-Marquardt minimization method [10] help to find the solution with few iterations of the whole processes.

Retrieval of trace gas concentration strongly depends on the atmospheric aerosol content. There are many methods in literature to retrieve aerosol information from DOAS measurement, especially [2,4,11]. Most of them make use of simultaneous measurement of O_4. The adopted "O_4 method" is described in [1] and in [2]. It consist in the simulation, with a RTM, of the O_4 DOAS measurements. According to its known [1] atmospheric concentration, the O4 measured slants, sensible to the variation of aerosol concentration, provide the required information. O_4 has different absorption bands along the UV/visible region of EM spectrum: each line is suitable in supplying aerosol properties in the absorption region of the target gases. The NO_2 profile is hence obtained using the measured spectra in the 436 – 495nm spectral range, in order to include the absorption line of O_4 at 477 nm. The same for SO_2 from 308 to 370nm, with the O_4 line at 360.5.

3. RESULTS

Since the purpose of this work is to give overall information on the algorithms used to get the NO_2 and SO_2 tropospheric profile, only few significant examples are presented. In order to show the typical shape of the retrieved profiles, they are averaged over different days with low pollution levels and with high pollution level.

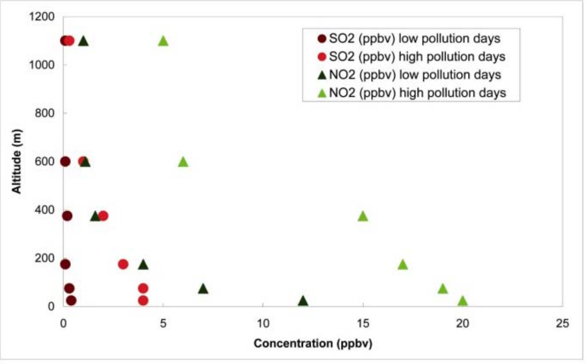

Figure 2. Example of SO_2 (red) and NO_2 (green) vertical profile obtained for days with low pollution and for days with high pollution levels. All profiles show a trend that decrease with altitude.

Figure 2 represents the concentrations of both gases as a function of altitude. Both profiles show a general decrease of the concentration as the altitude increase and this behaviour is maintained both for polluted and clean days

The NO_2 vertical tropospheric column value is calculated from the profile (NO2_IPR). This is obtained integrating the concentration values over the full altitude (1200m). The obtained values are then compared with the tropospheric column from OMI satellite data (NO2_SAT), available on www.TEMIS.nl [12]. A further validation procedure is performed calculating the column value retrieved from the 30° from the horizon line of sight, as described in [5] (NO2_30°).

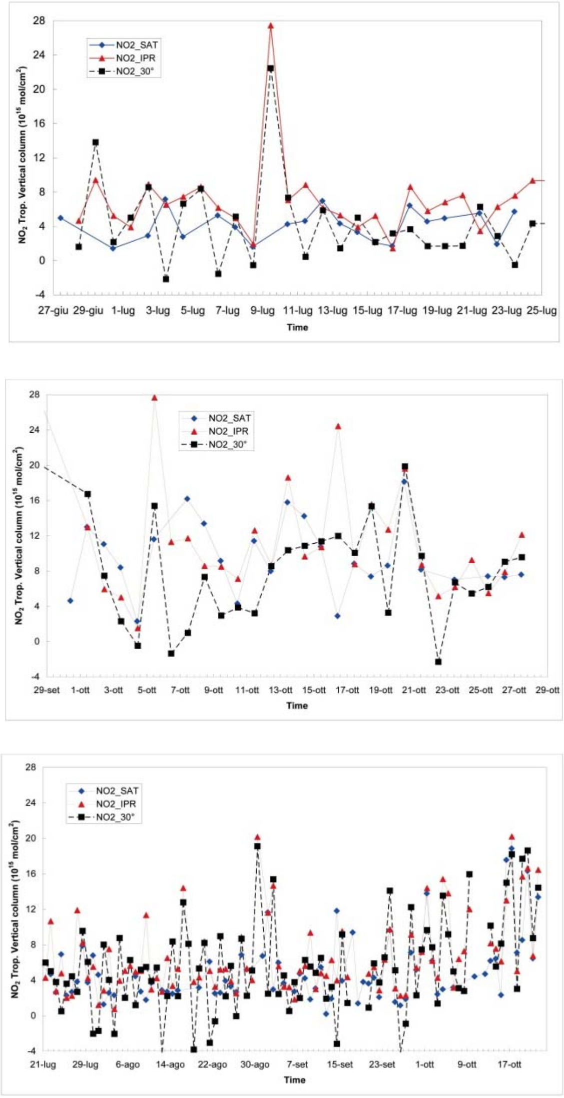

Figure 3. Time series of the tropospheric vertical column measured with the TROPOGAS spectrometer and with the satellite borne OMI sensor, during the three periods of measurements.

Figure 3 represents the comparison between: the NO_2 tropospheric vertical column calculated from the profiles (NO2_IPR) (red triangles), the column calculated from the 30° angle of site measurement (NO2_30°) (black squares) and the column provided by satellite (NO2_SAT) (blue diamonds). The comparison shows a sensible correlation (R^2=0.31) exemplified in the scatter plot in Figure 4. In addition, the correlation coefficient R^2 increases as the entire dataset (All data green; squares) is reduced excluding the days with cloud cover higher than 0.4 (Clear Sky: red circles), and excluding the OMI data with large swath angles [12] (Clear Sky high res.: blue diamonds).

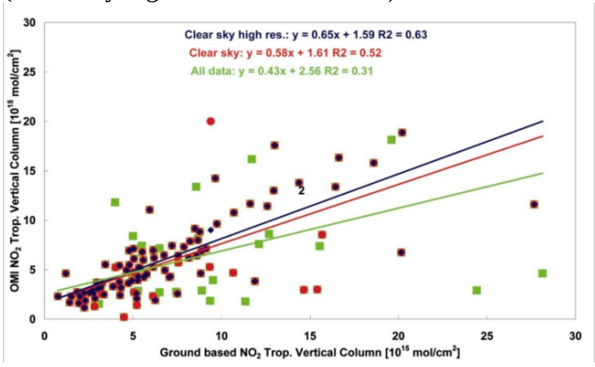

Figure 4. Scatter plot of NO_2 tropospheric vertical column as seen by the satellite and by the TROPOGAS spectrometer. Green squares represent the entire dataset, the red circles correspond to the clear sky data, and the blue data stand for those with high resolution overpass.

4. CONCLUSIONS

The method proposed demonstrates its applicability in detecting vertical profiles of NO_2 and SO_2. The particular place chosen for measurements (i.e. Venice in which diesel engine boats are the common transport media) permits also to obtain the SO_2 vertical distributions, not regularly measured because of their low concentrations in troposphere.

The obtained results show a high stratification well known in polluted places especially for NO_2. SO_2 profiles follow almost the same vertical shape of the NO_2 profiles, but with lower values.

The determination of the tropospheric NO2 vertical allows for the comparison with the value from OMI data (www.TEMIS.com). The results shows an improvement of the correlation coefficients when from the entire data set (with R^2=0.31), only the data obtained during clear sky days are considered, given a correlation coefficient of 0.52. Furthermore, if only the OMI data obtained for high resolution swath are considered the correlation increases to 0.63.

5. ACKNOWLEDGEMENT

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