VALIDATION OF SCIAMACHY NO_2 VERTICAL COLUMN DENSITIES WITH MT.CIMONE AND STARA ZAGORA GROUND-BASED ZENITH SKY DOAS OBSERVATIONS

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ABSTRACT

Ground-based zenith sky Differential Optical Absorption Spectroscopy (DOAS) measurements performed by means of GASCOD instruments at Mt. Cimone (44N 11E), Italy and Stara Zagora (42N, 25E), Bulgaria are used for validation of SCIAMACHY NO_2 *vertical column density (vcd)* of ESA SCI_NL product retrieved with 5.01 processor version. The results presented in this work regard satellite data for the July-December 2002 period. On this base it is concluded that during summer-autumn period the overall NO_2 *vcd* above both stations is fairly well reproduced by the SCIAMACHY data, while towards the winter period they deviate from the seasonal behaviour of NO_2 *vcd* derived at both stations.

1. INTRODUCTION

The design and assembly of individual instruments devoted to remotely exploration of the Earth atmosphere from the space include number of calibration and test procedures carried out during the pre-flight phase. The aim of these procedures is to simulate the space conditions under which the instruments will operate in orbit, e.g. sharp variations in temperature (sunlight-darklight parts of the orbit), different illumination levels within instrumental field of view (FoV), etc. and to check the behaviour of spaceborne sensors under circumstances expected in space. Nevertheless sophisticated equipment are deployed for such tasks, not all natural factors and processes which potentially can influence the quality of the spaceborne measurements can be completely reproduced in laboratory conditions. In order to verify the consistency of the satellite measurements regarding certain atmospheric parameters with those derived by other independent methods, dedicated and coordinated ground-based, aircraft, ship and balloon campaigns are organised in particular periods and regions. The results derived during these campaigns are considered as references for validation of the satellite data.
Ground-based zenith sky Differential Optical Absorption Spectroscopy (DOAS) measurements are considered as a powerful method for deriving of atmospheric content of wide number of minor gases playing important role in the atmospheric chemistry.

The advantage to deploy DOAS for validation tasks arise from the fact that it is largely adopted also for retrieving of the same atmospheric parameters from the satellite measurements. In particular, we have used for this study routine NO_2 DOAS measurements carried out at Mt. Cimone, and Stara Zagora Bulgaria.

2. INSTRUMENTAL SET-UP AND METHOD OF SATELLITE DATA VALIDATION

Both GASCOD instruments, deployed for the validation purposes, appear UV/VIS DOAS spectrometers measuring down-welling zenith scattered solar radiation during twilight period (SZA 75º-93º) within a narrow FoV of 1.1E-5 *sr* in automatic mode during all the year. Detected spectra are processed accordingly to DOAS method, [1,2,3,4,5 and references therein], applying several procedures: shift & stretch for spectral alignment, FFT smoothing, regression analysis (considering some “pseudo” absorbers as *Ring*, *polarization*, *Mie* and *Rayleigh* differential cross-sections into the master equation).

NO_2 slant column content is retrieved in the 406.5 nm – 465.0 nm spectral range, where absorption features of this gas are well pronounced. The instrumental accuracy and precision is evaluated through laboratory measurements by means of gas cell (Ø150 mm x 1000mm) and through the participation in several intercomparison campaigns. On this base it is concluded that the accuracy and the precision of retrieved NO_2 slant column at 90° SZA is better than 10% and 5% respectively. For more details about the instrumental performances and data processing can be find in [6].

The conversion of the retrieved NO_2 slant columns into *vcd* requires relevant air-mass factor evaluation, which was carried out by means of an atmospheric radiation

Proceedings of the Second Workshop on the Atmospheric Chemistry Validation of ENVISAT (ACVE-2)
ESA-ESRIN, Frascati, Italy, 3-7 May 2004 (ESA SP-562, August 2004) EPOSCIK

transfer model, (AMFCO) developed at ISAC/CNR, [7].

3. STRATOSPHERIC NO_2 PHOTOCHERMISTRY

NO_2 is a photochemically active specie and during the day its stratospheric content is controlled mainly by photodissociation loss

(1) $NO_2 + h\nu \rightarrow NO + O$ ($\lambda < 420$ *nm*),

and production via

(2) $N_2O + h\nu \rightarrow N_2 + O(^1D)$

(3) $O(^1D) + N_2O \rightarrow 2\,NO$

(4) $NO + O_3 \rightarrow NO_2 + O_2$

Both processes strongly depend on the available solar UV radiation, so NO_2 *vcd* exhibits diurnal and seasonal variations. The interconversion between NO and NO_2 is enough fast, with a time scale of a few minutes at 20 km to a few seconds at 30km, so photochemical steady-state equilibrium takes place at these altitudes in middle latitudes for solar zenith angles ≤ 80°. Around SZA = 90° the fast variation of the available solar radiation leads to relevant changes of the local photochemistry, so direct correlation of remote sensing satellite measurements with ground-based zenith sky DOAS measurements @SZA=90° are not feasible for validation purposes.

However, this difficulty for the validation procedure, requiring certain temporal and spatial coincidence of the measurements performed both from the space and the ground can be overcome taking into account some theoretical considerations. *Lambert et al.* [8] have carried out model studies developing an approach for better assessment and validation of SCIAMACHY (further referred to SCIA) NO_2 nadir measurements. Such procedure has already been applied to validate former version of SCIA NO_2 *vcd* product using Mt.Cimone and Stara Zagora data [9]. Here we applied this approach, but interpolating linearly the diurnal increasing of NO_2 *vcd* for the time of ENVISAT overpass using NO_2 a.m. *vcd* and NO_2 p.m. *vcd* @SZA = 80°:

$$(5)\quad NO_{2\,gb@op} = NO_{2am@80^\circ} + (NO_{2pm\,@80^\circ} - NO_{2am\,@80^\circ}) . (t_{pm@80^\circ} - t_{am@80^\circ}) / (t_{gb80\,@op} - t_{am\,@80^\circ}),$$

where $_{gb@op}$ indicates ground-based measurement during the ENVISAT overpass, $_{am@80^\circ}$ and $_{pm@80^\circ}$ relate to a.m and p.m NO_2 slant columns, t is the local time of the measurements.

The reason of this choice arise from the attempt to draw as near as it is possible both observational geometries, from the space (nadir) and from the ground (zenith). In fact, SCIA nadir measurements intersect the stratosphere and the troposphere vertically and hence the contribution of these layers to the NO_2 *vcd* is not the same as those derived from ground-based zenith sky measurements @SZA = 90°. Under such geometry derived from the ground NO_2 slant column, used subsequently to calculate NO_2 *vcd* represent absorption of the solar radiation by nitrogen dioxide mainly in the stratosphere. In general, we consider the problem of the geometry as a very important issue and further efforts are required to evaluate more accurately the most appropriate solar zenith angle for ground-based measurements devoted to satellite data validation. Here we would like to underlie that the retrieval error of NO_2 ground-based measurements performed at both stations @SZA = 80° is still within overall instrumental accuracy for the days selected for this study.

4. RESULTS AND DISCUSSION

The availability of enough satellite data is a crucial factor for confidential statistical assessment if they can reproduce adequately the real atmospheric parameters. One way to get required number of data is to increase the range around given ground-base station where the air masses are probed from the space.

A such approach however, can create additional problems arising from the very different environmental and atmospheric conditions, which eventually could take place within each single spaceborne instrumental nadir pixel, so derived correlation between ground-based and satellite measurements became subsequently not enough representative.

For instance, the increasing of range more than 50 km away from Mt. Cimone station leads to including of SCIA nadir pixels sampled above Po valley, known as one of European hot spots due to its high tropospheric NO_2 pollution [10]. On the other hand restricting the range we got very limited number of available satellite measurements. Finally we set a range of 75 km around Mt.Cimone station for this study as compromise. It allows us to individuate in the examined period 70 SCIA high resolution nadir pixels and on the other hand to have reduced impact from the Po valley.

In Fig. 1 both ground-based and satellite measurements related to the selected area are shown. The SZA corresponding to the middle of the integration time at the top of the atmosphere is plotted too.

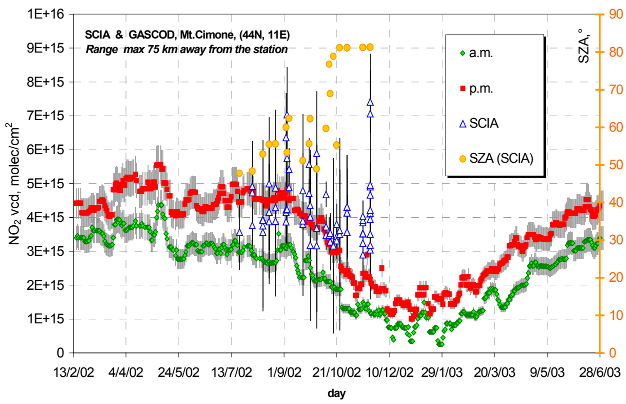


Figure 1. Mt.Cimone NO_2a.m. and NO_2p.m. *vcd* @SZA=90° data series. Retrieval errors for both data series is shown in grey colour. The SCIA NO_2 *vcd* for each nadir pixel is plotted with its own error bar.

In Fig. 2, where daily averaged SCIA data are plotted, one can note that they drift far from NO_2 a.m. *vcd* data towards the winter period.

Until 24/08/2002 SCIA NO_2 *vcd* data remain within Mt.Cimone a.m. - p.m. range, while after that they almost coincide with NO_2 p.m. or are higher. Only in two cases, 21/07/2002 and 24/10/2002, SCIA data are close to NO_2 a.m. values, as can be expected from the overall considerations regarding the photochemistry at middle latitudes.

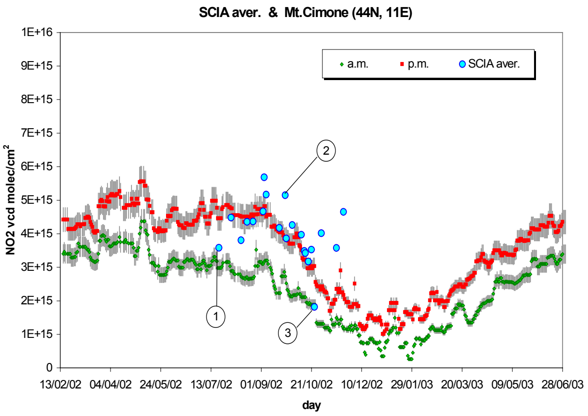


Figure 2. As in Fig 1, but SCIA NO_2 *vcd* data are daily averaged. Points 1, 2 and 3 depict three particular days with lightning activity (see text for details)

Further, we applied a linear interpolation of the daily ground-based measurements @SZA=80° according (5). A scatter plot of both data series is shown in Fig.3, where SCIA overestimation of NO_2 *vcd* is evident. This overestimation is higher for the lower NO_2 *vcd* values, which correspond to the winter period. Analysing all available data for the selected range of 75 km, we found mean SCIA NO_2 *vcd* overestimation of 33 % over this station during July-December 2002 period.

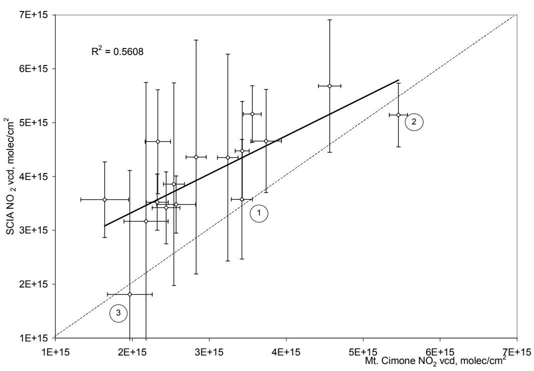
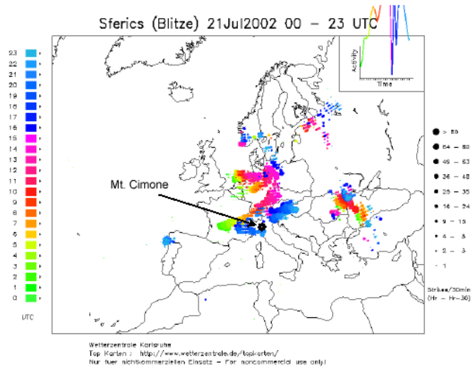


Figure 3. Scatter plot of Mt.Cimone and SCIA NO_2 *vcd* points 1, 2 and 3 are considered significantly influenced by lightning NO_2 production

There are three characteristic points very near to the graph diagonal, shown as circled numbers. Point 1 (21st July,'02), during this day and the day before lightning activity took place around Mt.Cimone station, (Fig 4), affecting mainly the tropospheric part of NO_2*vcd*. This is well pronounced in the p.m. ground-based measurements of NO_2 slant columns (not shown here), with subsequent effects on the calculated NO_2 *vcd*.



Figigure 4. Atmospheric lightning around Mt.Cimone for 21st July 2002, [11].

Similar effect can also be assigned to point 2 (25 Sep. 2002), when lightning appeared within the examined area in the early morning and during ENVISAT overpass, Fig 5.

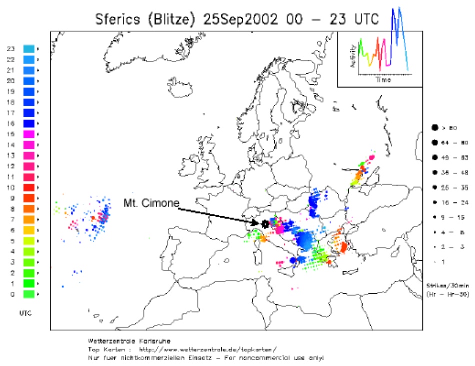


Figure 5. Atmospheric lightning around Mt.Cimone for 25th Sept 2002, [11].

Regarding point 3, we suppose also that these measurements are influenced by the lightning activity afternoon on 23 Oct.'02 around Mt. Cimone station and in the morning of 24 Oct.'02 easterly from it. In nadir mode SCIA probes vertically the air masses near to Mt.Cimone station and it is plausible that the satellite measurements are affected by the additional production of NO_2 due to the lightning activity not in the same manner as the ground-based observations. There are several factors plying in this regard: the differences of the instrument's FoVs, time differences of the atmosphere probing, air mass transport phenomena, etc.

Before to draw some conclusions regarding the quality of the SCIA NO_2 *vcd* data, we examined if the cloud appearance within its FoV could be the reason for aforementioned drift. Such verification is based on the fact that towards winter period the cloud appearance increases above this station. We examined visually relevant METEOSAT [12] VIS images in order to get overall impression about the clouds presence during the measurements. For a quantitative evaluation we used the *cloud_fraction* parameter for each SCIA nadir pixel and we correlated it to the NO_2 *vcd* for the same pixel.

As an example a scatter plot for two days is shown in Fig 6*a,b*. Fairly weak increasing of SCIA NO_2 *vcd*, within the experimental error, with increasing of the cloud fraction, can be noted.

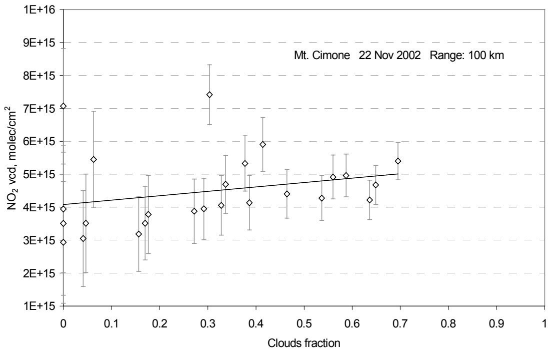


Figure 6*a*. SCIA NO_2 *vcd* vs. corresponding *cloud*_fraction for 22nd Nov 2002 nadir pixels. The range has been increased up to 100 km in order to get larger variety of *cloud_fraction* indexes for this day.

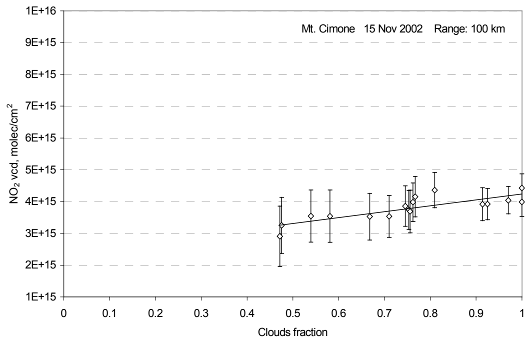


Figure 6*b*. As in Fig. 6*a*, but for day 15th Nov 2002

Regarding the observation performed at Stara Zagora station we increased the radius of the area probed from the space up to 150 km, because the choice of range of 75 km, as that for Mt.Cimone station, limits to very few available SCIA data. Nevertheless this, we find insufficient number of SCIA data (set A in Fig.7), so it constrained us to enlarge the radius of the examined area up to 450 km.

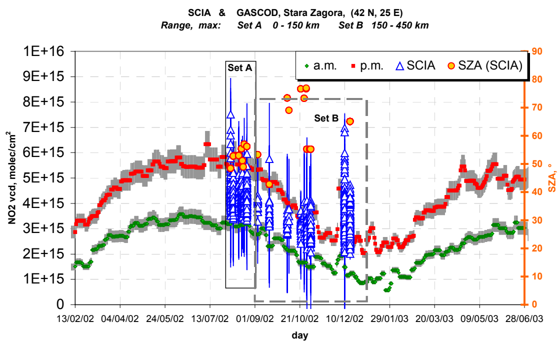


Figure 7. Stara Zagora NO_2a.m and NO_2p.m *vcd* @SZA=90° data series. Retrieval errors for both data series is shown in grey colour. The available SCIA NO_2 *vcd* for each nadir pixel is plotted with its own error bar.

Selected satellite data have been daily averaged for each overpass and plotted in Fig.8. A drift of SCIA data far form ground-based data is well pronounced towards the winter period. This overall behaviour is very similar to that derived at Mt.Cimone station.

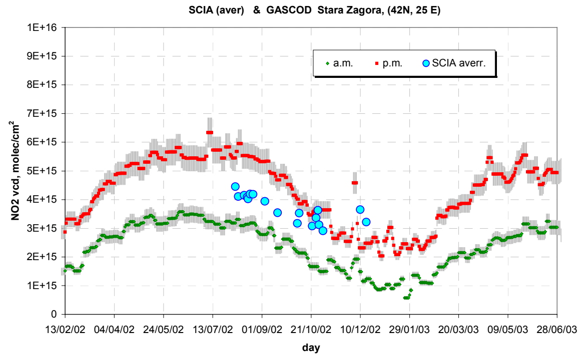


Figure 8. As in Fig 7, but SCIA NO_2 *vcd* data are daily averaged.

We have applied a linear interpolation according (5) in order to get NO_2 *vcd* measured at this station for the time of ENVISAT overpasses. A scatter plot of satellite and ground-based data series is shown in Fig 9, where SCIA overestimation of NO_2 *vcd* is clearly pronounced.

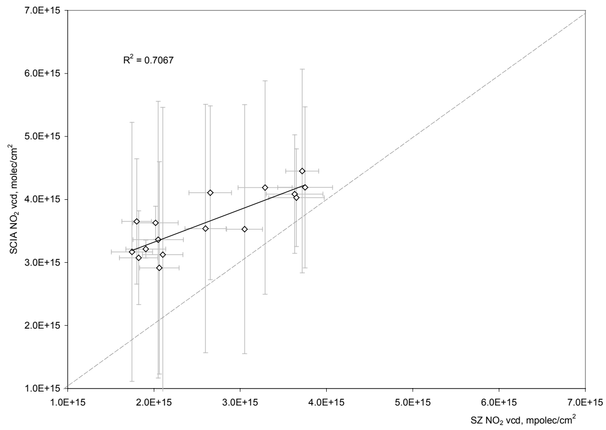


Figure 9. Stara Zagora vs. SCIA NO_2 *vcd*

SCIA NO_2 *vcd* and *cloud_fraction* around Stara Zagora station have been correlated to verify if clouds can be considered as a potential factor contributing to the observed drift. The results from this analysis, (e.g. Fig 10*a,b*) do not confirm clearly that SCIA NO_2 *vcd* are substantially affected for a wide interval of the *cloud_fraction* parameter ranging from 0.0 to 0.8.

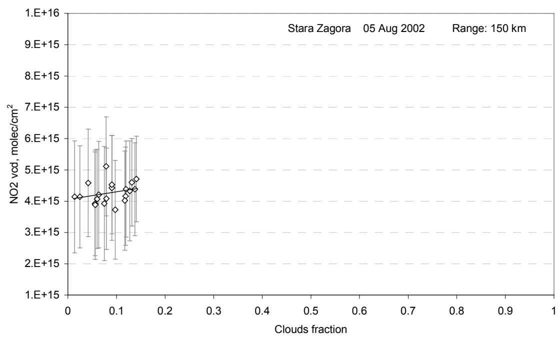


Figure 10*a*. SCIA NO_2 *vcd* and corresponding *cloud_fraction* for given pixel over Stara Zagora, 5th Aug. '02.

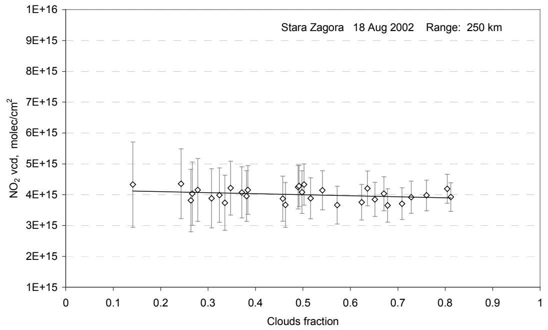


Figure 10*b*. As Fig. 10*a* but for 18th Aug ′02

The analysis of the SCIA NO_2 *vcd* above Stara Zagora station shows mean overestimation of 29% for the all examined period and 24% for July-September period.

5. CONCLUSIONS:

The very limited data SCIA set constrain us to draw some general conclusions regarding its ability to reproduce NO2 *vcd* derived by means of ground-based zenith sky DOAS technique. However some preliminary statements can be outlined.

- Until the beginning of the autumn period, for both stations, SCIA reproduce fairly well the seasonal NO_2 *vcd* behaviour and after that it drifts far to higher values.
- For July-September period SCIA overestimates NO_2 *vcd* over Stara Zagora of about 24% while for Mt. Cimone station SCIA overestimation is higher.
- The clouds appearance within the areas under interest is considered to be not a factor for revealed experimental discrepancies between examined data series. The influence of the clouds on SCIA NO_2 *vcd*, if conformed, can't explain revealed discrepancy from ground-based measurements. More depth studies are required in this regard.
- Precise comparison of ground-based and satellite data series requires detailed information about existence and contribution of another factors or processes which potentially can modify NO_2 vertical profile, (e.g. local lightning production, tropopause foldings, transport toward both stations of air masses with polar or subtropical origin, etc.) and hence to influence the correlation between ground-based and satellite measurements.

ACKNOWLEDGMENTS:

This work is funded partially by the Italian Space Agency (ASI); CNR (Italy) - BAS (Bulgaria) bilateral Project 13; EU QUILT project.

The author I.Kostadinov undertook this work with the support of the "ICTP - Programme for Training and Research in Italian Laboratories, Trieste, Italy"; The author Daniele Bortoli was financially supported by the "Subprograma Ciência e Tecnologia do 3° Quadro Comunitário de Apoio"

We thank Mt. Cimone station staff and in particular Paolo Bonasoni, Franco Evangelisti, Francescopiero Calzolari, Ubaldo Bonafè and Polo Cristofanelli for their fruitful collaboration.

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