Measurements of Tropospheric NO₂ in Romania Using a Zenith-Sky Mobile DOAS System and Comparisons with Satellite Observations

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Abstract: In this paper we present a new method for retrieving tropospheric NO₂ Vertical Column Density (VCD) from zenith-sky Differential Optical Absorption Spectroscopy (DOAS) measurements using mobile observations. This method was used during three days in the summer of 2011 in Romania, being to our knowledge the first mobile DOAS measurements performed in this country. The measurements were carried out over large and different areas using a mobile DOAS system installed in a car. We present here a step-by-step retrieval of tropospheric VCD using complementary observations from ground and space which take into account the stratospheric contribution, which is a step forward compared to other similar studies. The detailed error budget indicates that the typical uncertainty on the retrieved NO₂ tropospheric VCD is less than 25%. The resulting ground-based data set is compared to satellite measurements from the Ozone Monitoring Instrument (OMI) and the Global Ozone Monitoring Experiment-2 (GOME-2). For instance, on 18 July 2011, in an industrial area located at 47.03°N, 22.45°E, GOME-2 observes a tropospheric VCD value of $(3.4 \pm 1.9) \times 10^{15}$ molec./cm², while average mobile measurements...
in the same area give a value of $$(3.4 \pm 0.7) \times 10^{15} \text{ molec./cm}^2$$. On 22 August 2011, around Ploiesti city (44.99°N, 26.1°E), the tropospheric VCD observed by satellites is $$(3.3 \pm 1.9) \times 10^{15} \text{ molec./cm}^2$$ (GOME-2) and $$(3.2 \pm 3.2) \times 10^{15} \text{ molec./cm}^2$$ (OMI), while average mobile measurements give $$(3.8 \pm 0.8) \times 10^{15} \text{ molec./cm}^2$$. Average ground measurements over “clean areas”, on 18 July 2011, give $$(2.5 \pm 0.6) \times 10^{15} \text{ molec./cm}^2$$ while the satellite observes a value of $$(1.8 \pm 1.3) \times 10^{15} \text{ molec./cm}^2$$.

**Keywords:** DOAS; spectrophotometer; nitrogen dioxide; mobile measurements

## 1. Introduction

Nitrogen dioxide (NO$_2$) is an important trace gas in the photochemistry of Earth’s atmosphere. In the stratosphere NO$_2$ plays a key role as a catalyst of the ozone destruction [1]. In the troposphere NO$_2$ is involved in the tropospheric ozone formation, having also a contribution to radiative forcing [2]. The main sources of NO$_2$ are combustion of fossil fuels, biomass burning, lightning and microbiological processes in the soil [3]. Using remote sensing from space, the lifetime of tropospheric NO$_2$ was estimated to be about 6 h in summer and 18–24 h in winter in mid-latitude industrialized regions [4].

Many studies show that exposure to high NO$_2$ concentrations can create or aggravate respiratory or coronary diseases [5,6]. NO$_2$ has seasonal variations which are both due to natural and anthropogenic causes [7].

The Differential Optical Absorption Spectroscopy (DOAS) technique [8,9] is a well established method that has been successfully applied to NO$_2$ monitoring from ground and space. One of the first applications of DOAS was dealing with ground-based stratospheric and tropospheric NO$_2$ measurements from zenith-scattered light observation [10,11]. Nowadays DOAS measurements are performed from a number of mobile platforms such as cars [12–15], balloons [16], ships [17], airplanes [18,19]. DOAS has also been used in satellite experiments such as SCIAMACHY [20], OMI [21] and GOME-2 [22] instruments, providing key observations to characterize NO$_2$ at the global, regional and even at the urban scale [23].

Cars represent a cheap and accessible platform to perform mobile DOAS measurements. Several studies have been performed in different parts of the world, e.g., China [12], Mexico [13], USA [15], Germany [24], India [25], etc. These studies were focused on quantification of emissions of different trace gases by megacities (e.g., Delhi) or industrial plants.

In this paper we present the retrieval of tropospheric NO$_2$ vertical column density (VCD) from zenith-sky mobile DOAS measurements using complementary observations from ground and space performed in Romania in the summer of 2011. In the next section the experiment and the methodology of tropospheric NO$_2$ VCD retrieval are introduced. The results of mobile DOAS measurements, their error analysis, and comparison with satellite observations are then presented in Section 3, followed by Conclusions.
2. Methodology

2.1. Experimental and Instrumental Descriptions

Mobile DOAS zenith-sky measurements were performed in Romania during three days in summer 2011: July 18, July 28 and August 22. The measurements covered about 800 km in different regions of the country, including urban, rural and industrial areas (Figure 1). All measurements were performed under clear sky or mostly clear sky conditions. The time interval of measurements, the distance traveled and the main cities on road route are presented in Table 1.

![Figure 1](image_url). The tracks of mobile DOAS measurements performed in Romania.

| Day       | Time Interval UT | Distance Traveled | Main Cities on Road Route                                      |
|-----------|------------------|-------------------|----------------------------------------------------------------|
| 18 July   | 7.23–16.22 h     | 500 km            | Oradea (47.05°N, 21.94°E)                                      |
|           |                  |                   | Cluj-Napoca (46.76°N, 23.60°E)                                 |
|           |                  |                   | Targu Mures (46.54°N, 24.55°E)                                 |
|           |                  |                   | Sighisoara (47.05°N, 21.94°E)                                 |
|           |                  |                   | Brasov (45.65°N, 25.60°E)                                     |
| 28 July   | 9.99–10.84 h     | 30 km             | Galati (45.43°N, 28.03°E)                                     |
|           |                  |                   | Braila (45.26°N, 27.95°E)                                     |
| 22 August | 10.78–14.12 h    | 250 km            | Ploiesti (44.94°N, 26.03°E)                                   |
|           |                  |                   | Buzau (45.15°N, 26.81°E)                                      |
|           |                  |                   | Braila (45.26°N, 27.95°E)                                     |
|           |                  |                   | Galati (45.43°N, 28.03°E)                                     |

Besides mobile measurements, a static DOAS experiment took place on 6 October 2011, at twilight-sunrise in a rural area close to Galati city.
The mobile DOAS instrument used in this work is based on a compact Czerny-Turner spectrometer (AvaSpec 2048 USB2, of 175 × 110 × 44 mm dimensions and 716 g weight) placed in a car. The spectral range of the spectrometer is 200–750 nm with 1.5 nm resolution (FWHM) with a focal length of 75 mm. The entry slit is 50 μm and the grating is 600 L/mm, blazed at 300 nm. The CCD detector is a Sony2048 linear array with a Deep-UV coating for signal enhancement below 350 nm. A flexible device (a piece of wood with a hole cached in a small metallic plate), mounted on the top of the road vehicle, holds the telescope achieving a 1.2° field-of-view with fused silica collimating lenses. The spectrometer is connected to the telescope through a 400 μm chrome plated brass optical fiber. Each spectrum is recorded by a laptop and georeferenced by a GPS receiver. The spectrometer and the GPS receiver are powered by the laptop USB ports. The entire set-up is powered by 12 V of the car through an inverter. Each measurement is a 5-second average of 10 scans accumulations at an integration time between 4–12 ms. The instrument was adapted from an instrument developed at BIRA-IASB [18]. Figure 2 presents the instrumental set-up.

![Figure 2. The mobile DOAS system.](image)

2.2. Determination of Tropospheric Vertical Columns of NO₂

The analysis of the zenith-sky spectra was performed using the QDOAS software [26], a program dedicated to the DOAS retrieval of atmospheric trace gases from ground-based and satellite measurements. The NO₂ column density was retrieved in the spectral region 425–500 nm where NO₂ has strong absorption lines. Absorption of O₃, H₂O and O₄ can also be detected in the same region. The cross sections of NO₂ at 298 K and 220 K [27], O₃ [28], O₄ (http://www.aeronomie.be/spectrolab/o2.htm) and H₂O [29] were included in the spectral fitting process. The “Filling-in” effect on Fraunhofer lines, also known as the Ring effect, originating from the rotational Raman scattering of molecular oxygen and nitrogen [30] was corrected by including into the fit a synthetic Ring spectrum calculated with QDOAS. Also a fifth degree polynomial representing the contribution of broad-band absorption in the atmosphere (Rayleigh and Mie scattering) was used in the DOAS analysis. The result of the DOAS fit is a Differential Slant Column Density (DSCD) of NO₂ which is the difference between the slant column densities in the measured spectra (SCD) and in the Fraunhofer reference spectrum (SCD_ref).
In our case, the tropospheric NO\textsubscript{2} VCD retrieval from zenith-sky observations, or the mobile DOAS measurement results, involves complementary ground-based and satellite measurements. Determination of the NO\textsubscript{2} amount in SCD\textsubscript{ref} is required in order to determine the tropospheric NO\textsubscript{2} VCD. Another important parameter is the air mass factor (AMF) which is needed to convert the resulted slant columns to vertical columns. The AMF is defined as the ratio between SCD and VCD (Equation (1)):

\[ AMF = \frac{SCD}{VCD} \]  

(1)

The total slant column density in a measured spectrum (SCD\textsubscript{meas}) is defined by Equation (2):

\[ SCD_{\text{meas}} = DSCD + SCD_{\text{ref}} \]  

(2)

where the NO\textsubscript{2} content in the Fraunhofer reference spectrum or SCD reference (SCD\textsubscript{ref}) is unknown.

Stratospheric and tropospheric content of NO\textsubscript{2} contribute to the measured slant column density, according to:

\[ AMF_{\text{tropo}} \times VCD_{\text{tropo}} + AMF_{\text{strato}} \times VCD_{\text{strato}} = DSCD_{\text{meas}} + SCD_{\text{ref}} \]  

(3)

Thus the VCD of NO\textsubscript{2} in the troposphere is given by:

\[ VCD_{\text{tropo}} = \frac{DSCD_{\text{meas}} + SCD_{\text{ref}} - AMF_{\text{strato}} \times VCD_{\text{strato}}}{AMF_{\text{tropo}}} \]  

(4)

where AMF\textsubscript{strato} and AMF\textsubscript{tropo} are the stratospheric and tropospheric AMFs respectively.

2.2.1. Deduction of SCD\textsubscript{ref}

A common way to quantify the SCD\textsubscript{ref} is to use a Langley plot which is the graphical representation of DSCD at twilight versus the associated AMF [31]. By applying a linear fit to the resulting curve the slope gives the VCD and the intercept gives the SCD\textsubscript{ref}, as shown in Equation (5):

\[ DSCD = VCD \times AMF - SCD_{\text{ref}} \]  

(5)

For NO\textsubscript{2}, due to the rapid variation of the NO\textsubscript{2} concentration in the stratosphere at twilight, a photo-chemically modified Langley-plot is required [31–33]. We thus used scaled AMFs calculated using the radiative transfer model (RTM) UVspec/DISORT [34] coupled to the photochemical box-model PSCBOX [35–37]. Both box-model and RTM have been validated through several comparison exercises [36–39]. For the present study, the box-model PSCBOX is daily initialized with chemical and meteorological fields extracted from the 3-D chemical transport model (CTM) SLIMCAT [40] for the Jungfraujoch station (46.5°N, 8°E) in Switzerland which is similar in latitude to the locations of the mobile DOAS performed in Romania.

A spectrum with a low NO\textsubscript{2} content recorded on 18 July 2011 at 8.82 UT and SZA = 33° was selected to represent and to determine the NO\textsubscript{2} amount in the reference spectrum. The reference spectrum was selected after a pre-analysis of DSCDs with a random spectrum. The reference spectrum was recorded in a clean area in forested mountains, Transylvania (46.93°N, 22.83°E). The stratospheric contribution in this spectrum is supposed to be small considering the small SZA. All spectra presented
in this paper have been analyzed with this spectrum. The benefits of using a single reference spectrum consist in avoiding different systematic errors which could affect the analysis process [41].

The NO\textsubscript{2} amount in the reference spectrum was obtained from ground-based zenith-sky measurements at sunrise on 6 October 2011. Figure 3 shows the photo-chemically corrected Langley plot for the SZA interval 90°–80°. The intercept of the corresponding straight line, representing SCD\textsubscript{ref} and derived by linear least-squares regression, was found to be $6.48 \pm 0.36 \times 10^{15}$ molec./cm\textsuperscript{2}.

Figure 3. The Langley-plot for SZA 90°–80° of measurements on 6 October 2011 with respect to a reference spectrum measured on 18 July 2011.

2.2.2. Deduction of VCD\textsubscript{strato}

Two methods for the determination of the stratospheric NO\textsubscript{2} are described below. The first method is based on the derivation of stratospheric VCDs from measurements at sunrise by using the Langley-plot analysis presented in [42]. The authors used sunrise/sunset observations analyzed with a reference spectrum at 75°SZA (Equation (6)) which ensures that the potential impact of tropospheric NO\textsubscript{2} variation in the Langley-plot analysis is reduced. This method can be successfully applied for sunrise/sunset observations performed in less polluted areas. Unfortunately it cannot be used for the retrieval of tropospheric NO\textsubscript{2} from our mobile measurements because these were not performed at twilight, but during daytime. However, the above method was used to infer stratospheric content of NO\textsubscript{2} using the static DOAS measurements on 6 October 2011. The AM variation of VCD\textsubscript{strato} including the sunrise of 6 October 2011 will be estimated by extrapolating the slope resulted from Langley-plot to the simulation of the PSCBOX-model. The VCD\textsubscript{strato} for 6 October 2011 was estimated at about $2.99 \times 10^{15}$ molec./cm\textsuperscript{2} (6:18 UTC):

\[ \text{VCD}_{75° \text{SZA}} = \text{DSCD}/(\text{AMF}_{\text{strato}} - \text{AMF}_{\text{strato, 75° SZA}}) \]

The second method to derive the stratospheric contribution is based on using the stratospheric NO\textsubscript{2} columns obtained from the OMI instrument onboard AURA satellite. The assimilated vertical stratospheric columns were extracted from DOMINO (Dutch OMI NO\textsubscript{2}) Level2 product [43]. The stratospheric NO\textsubscript{2} slant column from DOMINO is estimated by data-assimilation of OMI slant columns in TM4 chemistry-transport model. The selection of data satellite was made for an area with a radius with the half linear distance between the first and the last point of ground measurement.
Variation of stratospheric NO$_2$ in OMI data over Romania was found less than 5%. Table 2 lists the satellite overpass data sets that were used for the present analysis.

| Day           | Orbit Nr. | Overpass Time | Stratospheric VCD |
|---------------|-----------|---------------|-------------------|
| 18 July 2011  | 37,628    | 11:35 UT      | $4.49 \times 10^{15}$ molec./cm$^2$ |
| 28 July 2011  | 37,778    | 10:34 UT      | $3.96 \times 10^{15}$ molec./cm$^2$ |
| 22 August 2011| 37,413    | 12:05 UT      | $4.03 \times 10^{15}$ molec./cm$^2$ |
| 6 October 2011| 38,433    | 11:35 UT      | $3.39 \times 10^{15}$ molec./cm$^2$ |

Figure 4 compares the stratospheric VCD derived from the photo-chemically modified Langley-plot and from OMI. The diurnal variation of VCD$_{strato}$ was calculated by extrapolating data from OMI measurements to the simulation of the PSCBOX model. Stratospheric NO$_2$ columns from the DOMINO retrieval exceed the ground-based measurements by no more than $0.3 \times 10^{15}$ molec./cm$^2$. In a recent study [44], where DOMINO was compared with the SAOZ (Système d'Analyse par Observations Zénithal) instruments and the Network for the Detection of Atmospheric Composition Change (NDACC), a similar level of agreement was found.

Figure 4. Comparison of the stratospheric NO$_2$ between ground-based measurements and derived from OMI on 6 October 2011. The AM diurnal variation was simulated using the PSCBOX model.

Both methods presented in this chapter are suitable to retrieve the tropospheric NO$_2$ content but the first method requires observations around twilight which are missing for the days with mobile measurements. Therefore, in this work, the DOMINO-based method was used to estimate stratospheric NO$_2$.
2.2.3. AMFs Simulations

The AMFs simulations presented in this study were performed using the radiative transfer model (RTM) UVspec/DISORT. The RTM is based on the discrete ordinate method and deals with multiple scattering in a pseudo-spherical approximation. Given the wavelength, the observation’s geometry relative to the Sun and the atmospheric state, the model calculates the scattered radiance and the absolute SCD of molecular absorbers. For the tropospheric AMF simulations we used NO$_2$ profiles representative of Romania obtained from the CHIMERE model. The AMF$_{tropo}$ simulations were made by setting a grid of 10 km altitude and the wavelength for NO$_2$ simulation at 440 nm. Figure 5 shows the results of tropospheric AMFs simulations for the three days with road measurements in 2011.

**Figure 5.** The tropospheric AMFs simulations for the three days of road measurements.

3. Results and Discussions

Figure 6 presents the spatial variation of tropospheric NO$_2$ VCDs and the corresponding NO$_2$ slant columns measured on 22 August 2011. The comparison of the DSCD with the VCD$_{tropo}$ gives similar values around noon, which can be explained by the quasi vertical light path of solar photons through the atmosphere when the sun is high. Also this might indicate that a noon reference spectrum with a low NO$_2$ content can correct for stratospheric slant column [42]. After noon, the DSCD increasingly and linearly deviates from the VCD$_{tropo}$ at a rate of approximately 1% per degree of SZA. This is due the diurnal variation of stratospheric NO$_2$. 
Figure 6. Time series of (a) DSCD and Total SCD; (b) Stratospheric SCD and VCD and; (c) Tropospheric SCD and VCD for 22 August 2011.

3.1. Error Estimation

This section presents an analysis of the errors and of their propagation through the retrieval process. Each parameter used in the determination of tropospheric VCD has a contribution to the accuracy of the final retrieval. The error propagation on tropospheric VCD ($\sigma_{VCD}$) can be expressed by Equation (7):
\[ \sigma_{VCD}^{2} = \left( \frac{\sigma_{DSCD}}{AMF_{tropo}} \right)^2 + \left( \frac{\sigma_{SCD_{ref}}}{AMF_{tropo}} \right)^2 + \left( \frac{\sigma_{SCD_{strato}}}{AMF_{tropo}} \right)^2 + \left( \frac{SCD_{tropo}}{AMF_{tropo}^2} \cdot \sigma_{AMF_{tropo}} \right)^2 \]  \hspace{1cm} (7)

Note that this expression assumes that the different error sources are uncorrelated, which is justified by the different origins of these error sources, which are described below. A correlation between the error of the DSCDs and the error of SCD_{ref} might exist if the NO\textsubscript{2} cross section used in the DOAS fit is inaccurate, but this is not seen in our case. The error sources in our calculation are the following:

(a) The error on the DOAS fitting (\(\sigma_{DSCD}\)) is calculated by QDOAS software and was found to be generally less than \(1 \times 10^{15}\) molec./cm\(^2\).
(b) The error on the estimation of the slant column in the reference spectra (SCD_{ref}), which was obtained using a Langley plots (\(\sigma_{SCD_{ref}}\)), depends on the one hand on the NO\textsubscript{2} variation during twilight and on the other hand on the correct selection of the SZA interval for the AMF calculation used in the Langley plots. In our case, the error on the SCD_{ref} was calculated using the standard error formula for the case of simple linear regression.

The selection of an adequate SZA interval for the determination of SCD_{ref} is a critical issue. Table 3 shows that different SZA intervals used in the linear fitting may induce different values of intercepts. To rate the different possible choices, we consider the mean squared error (MSE) and the standard error of the linear regression. The interval with the smallest errors was selected as confidently representing the Langley plot. Using SZAs from 90° to 80°, the estimated \(\sigma_{SCD_{ref}}\) is of \(3.56 \times 10^{14}\) molec./cm\(^2\). As mentioned in Section 2.2.2, the measurements at large SZA are less contaminated by tropospheric NO\textsubscript{2}, On the other hand, when the sun is under the horizon, the available light is much reduced and the errors on the DOAS fit increase. The interval 90°–80° was chosen since it minimized the fit error.

| SZA     | 92°–80°  | 91.5°–80° | 90°–80°  | 91.5°–75° | 91.5°–72° | 90°–75°  |
|---------|---------|---------|---------|---------|---------|---------|
| Intercept (\(\times 10^{15}\)) | -9.98   | -8.51   | -6.48   | -5.77   | -5.07   | -4.31   |
| MSE (\(\times 10^{15}\))     | 2.36    | 1.51    | 0.89    | 1.74    | 1.75    | 1.10    |
| \(\sigma_{SCD_{ref}} (\times 10^{14})\) | 7.13    | 4.80    | 3.56    | 3.75    | 7.13    | 5.09    |

(c) The error on stratospheric SCD (\(\sigma_{SCD_{strato}}\)) is the uncertainty on the assimilated stratospheric slant column from DOMINO data product v2.0. This error is based on observation-forecast statistics [43–45] and is estimated to be \(0.25 \times 10^{15}\) molec./cm\(^2\).

(d) The AMF calculation can introduce important errors on the retrieval process of tropospheric VCDs. The tropospheric AMFs applied in this work were computed with DISORT using NO\textsubscript{2} profiles from the CHIMERE chemistry transport model over Romania. In [46] the \(\sigma_{AMF_{tropo}}\) uncertainties are estimated at 10%–20%, for SZA increasing from 20° to 85°. They use various input parameters for the radiative transfer simulation. Since their study presents an accurate description of AMF’s uncertainties, their estimations of the error on tropospheric AMFs were used here.
After analyzing each error source we find that the major source of error comes from the DOAS fit. Our calculations show that, for all mobile measurements, the typical uncertainty on the retrieved NO$_2$ tropospheric VCD is less than 25%.

As an additional selection criterion, O$_4$ absorption measurements performed together with NO$_2$ were used as an indicator for the variation of the radiative transport through the atmosphere [47]. In a clear sky atmosphere, the oxygen collisional dimer O$_4$ absorption varies with the square of the oxygen pressure [48] and is weakly dependent on temperature [49]. Analyzing the O$_4$ DSCDs resulting from the DOAS fit (Figure 7) the time variations of O$_4$ can therefore give an idea of the light path enhancement through the atmosphere.

**Figure 7.** Diurnal variations of O$_4$ DSCDs absorptions for clear sky or mostly clear sky conditions on (a) 18 July 2011; (b) 28 July 2011 and (c) 22 August 2011.

3.2. Comparison of Our Mobile Measurements with Satellite Data

In this section the tropospheric VCDs retrieved from mobile zenith-sky measurements are compared with the tropospheric VCDs derived from the nadir measurements of OMI and GOME-2 instruments, onboard the AURA and Metop-A satellites. Only pixels with the geographic center located below 20 km distance of mobile measurements for GOME-2 and respective 10 km for OMI were selected for comparison. The largest number of mobile measurements were made on 18 July 2011, but they could not be used for comparison with OMI observations because the satellite passed over Romania close to the West border of the country, while the ground measurements were performed inside the country, more than 50 km away from the closest satellite pixel. The only day
when matching observations from both satellites exist was 22 August 2011. In Figure 8 a color coded comparison between road measurements and GOME-2 observations made on 18 July 2011 is shown.

**Figure 8.** Color coded tropospheric NO$_2$ VCD for the Oradea-Cluj Napoca road measurements on 18 July 2011 (line) and GOME-2 tropospheric NO$_2$ VCDs for the same day (rectangles).

The next figure presents measurements of GOME-2, with a horizontal resolution of 40 × 80 km$^2$, mobile observations and the average of mobile observations according to pixel size of GOME-2. Satellite observations and averages of mobile measurements are accompanied by error bars. The background NO$_2$ satellite loading was considered to be the minimum observed by satellite, which is (1.8 ± 1.3) × 10$^{15}$ molec/cm$^2$.

The NO$_2$ background for mobile measurements was obtained by averaging the measurements between 22.8 and 23.1 longitude, where NO$_2$ is low and relatively constant. This gives (2.5 ± 0.6) × 10$^{15}$ molec./cm$^2$ which is close to the minimum observed by satellite.

After averaging the tropospheric NO$_2$ columns along the spatial extent of the satellite pixel, for a location centered on 47.03°N, 22.45°E which is influenced by emissions of two important cities, Oradea (47.05°N, 21.94°E) and Cluj-Napoca (46.76°N, 23.60°E), the NO$_2$ loadings were found to be similar. For this location the averaged mobile measurements amount to (3.4 ± 0.7) × 10$^{15}$ molec./cm$^2$ while GOME-2 observations indicate (3.4 ± 1.9) × 10$^{15}$ molec./cm$^2$. Figure 9 shows that satellite measurements in the pixels located at 22.2 and 23.4 longitude are significantly smaller than mobile measurements. The satellite cannot “see” NO$_2$ emissions from very small areas (e.g., NO$_2$ located around to the road with low traffic, small cities or villages) while mobile measurements can determine the NO$_2$ at a very small resolution comparing to GOME-2 observations (40 × 80 km$^2$). The area of measurements is generally “clean” of NO$_2$ being covered mostly by forested mountains. We believe that an increased number of measurements inside the GOME-2 pixels, away from point sources of NO$_2$, would reduce discrepancies after averaging the mobile measurements according to the size of the satellite pixel.
Figure 9. Comparison of tropospheric NO$_2$ VCD obtained from mobile DOAS zenith-sky measurements with GOME-2 observations (18 July 2011) and corresponding error bars.

In Figure 10 we present the color coded comparison between road measurements and OMI measurements for another day, 22 August 2011.

Figure 10. Color coded tropospheric NO$_2$ VCD for the Ploiesti - Galati road measurements (line) on 22 August 2011 and OMI tropospheric NO$_2$ VCDs (rectangles) for the same day.

Figure 11 shows the tropospheric NO$_2$ VCD derived from zenith-sky measurements corresponding to OMI and GOME-2 satellite observations, as a function of latitude. The first NO$_2$ peak of mobile measurements was recorded close to a power plant around Ploiesti city and the second one was recorded around a steel and iron factory which is close to the Galati city. Between these cities no other strong source for NO$_2$ emissions exists along the trajectory of the mobile measurements. The NO$_2$ background for mobile measurements is estimated at about $\left(3.5 \pm 0.6\right) \times 10^{15}$ molec./cm$^2$. The satellite instruments generally underestimate NO$_2$ content, especially in less polluted areas. However, the difference between satellite and mobile observations are reduced in areas where strong NO$_2$ sources are encountered.
Figure 11. Comparison of tropospheric NO\textsubscript{2} VCD deduced from mobile DOAS zenith-sky measurements with OMI and GOME-2 observations (22 August 2011) and the corresponding error bars.

The smoothing effect is significant even for OMI measurements with the finest resolution (13 × 24 km\textsuperscript{2}) for areas with localized NO\textsubscript{2} sources. For a better comparison we average the ground measurements according to the size of the OMI pixels. This reduces the differences between the two sets of measurements. For instance, at 11:10 UTC, around coordinates 44.9°N, 26.1°E, which corresponds to the industrial area of Ploiesti city, GOME-2 reports a NO\textsubscript{2} content of (3.3 ± 2.1) × 10\textsuperscript{15} molec./cm\textsuperscript{2}, OMI gives (3.2 ± 3.2) × 10\textsuperscript{15} molec./cm\textsuperscript{2} and the average of mobile measurements shows (3.8 ± 0.8) × 10\textsuperscript{15} molec./cm\textsuperscript{2}.

Figure 12. The NO\textsubscript{2} “city center effect” in Braila town figured with mobile zenith-sky DOAS measurement on 28 July 2011.

Figure 12 shows a “zoom” inside of an OMI pixel made by mobile DOAS measurements in Braila city on 28 July 2011. Braila city is a relatively small city (77.9 km\textsuperscript{2}), whose main source of atmospheric pollution is due to local transportation. The maximum mobile tropospheric NO\textsubscript{2} column recorded is (2.5 ± 0.5) × 10\textsuperscript{16} molec./cm\textsuperscript{2} and its corresponding average for an OMI pixel is (4.9 ± 1.2) × 10\textsuperscript{15} molec./cm\textsuperscript{2}. For the same area, OMI reports a column of about
(2.4 ± 1.3) \times 10^{15} \text{ molec./cm}^2.\ The significant difference between OMI and mobile DOAS measurements is probably caused by the smoothing effect inside the pixel. The total surface of an OMI pixel is 312 km² which is 4 times larger than the area where local transportation increases the NO₂ content. The size of the satellite pixel and the magnitude of the hot-spot are most likely responsible for these discrepancies.

4. Conclusions

Zenith-sky mobile DOAS measurements were performed in Romania over large areas during three days in summer 2011. These were complemented by static measurements at twilight. A detailed method for retrieval of tropospheric NO₂ VCDs using ground-based and satellite observations is presented. This method presents three steps. First the NO₂ amount in the reference spectrum is determined from ground-based measurements performed at twilight-sunset, using a photo-chemically modified Langley plot. The second step consists in determining the stratospheric NO₂ SCD content by means of the assimilated vertical stratospheric column from the satellite DOMINO NO₂ product. By comparing stratospheric NO₂ VCDs derived from DOMINO with twilight observations for the morning of 6 October 2011, it is found that the stratospheric NO₂ from DOMINO exceeds the ground-based measurements by no more than 0.3 \times 10^{15} \text{ molec./cm}^2. To determine the diurnal variation of stratospheric NO₂, PSCBOX model simulations were used. Finally, the tropospheric VCD was determined using a tropospheric AMF calculated with the RTM UVspec/DISORT, using NO₂ profiles representative of Romania obtained from the CHIMERE model. Error propagation on tropospheric VCD was estimated to be less than 25%.

The comparison of the mobile DOAS measurements with results of OMI and GOME-2 instruments shows that satellite-based measurements generally underestimate ground-based mobile observations for areas with VCD NO₂ background smaller than 5 \times 10^{15} \text{ molec./cm}^2. In contrast, the difference between mobile observations and satellite measurements is reduced in areas with strong NO₂ emissions. Averaging mobile measurements in order to better match the horizontal extent of satellite pixels nearby a NO₂ pollution source on 18 July 2011 gives (3.4 ± 0.7) \times 10^{15} \text{ molec./cm}^2, while the corresponding result of GOME-2 for the same area gives shows (3.4 ± 1.9) \times 10^{15} \text{ molec./cm}^2. On 22 August 2011, around Ploiesti city (44.99°N, 26.1°E), GOME-2 measures a NO₂ content of (3.3 ± 1.9) \times 10^{15} \text{ molec./cm}^2, OMI gives (3.2 ± 3.2) \times 10^{15} \text{ molec./cm}^2 while the corresponding average of mobile measurements is (3.8 ± 0.8) \times 10^{15} \text{ molec./cm}^2. Over “clean areas” with forested mountains, the average of ground measurements on 18 July 2011 gives (2.5 ± 0.6) \times 10^{15} \text{ molec./cm}^2 while the satellite observations show (1.8 ± 1.3) \times 10^{15} \text{ molec./cm}^2.

One of the possible future applications for mobile measurements such as presented in this work would be to derive more accurate NO₂ emissions data around point sources. The comparison of mobile measurements with simultaneous Multi-Axis (MAX-) DOAS measurements and satellite observations will be the subject of a future paper.
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