MEASUREMENTS OF TROPOSPHERIC NO_2 IN A ROMANIAN REGION USING A MOBILE DOAS SYSTEM

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Abstract: This paper presents tropospheric NO_2 measurements made in the South-Eastern part of Romania, during several days in the summer season, using a portable DOAS (Differential Optical Absorption Spectroscopy) system placed on a motor vehicle. A GPS (Global Positioning System) device was used for location tracking. The measurements were made in zenith view and the NO_2 DSCD (Differential Slant Column Density) was determined with QDOAS software package developed by the Belgian Institute for Space Aeronomy. The aim of this study is to investigate short-term and local variations of NO_2 loading dependence on location and proximity to traffic or industrial areas.

Keywords: nitrogen dioxide, mobile DOAS system

1 Introduction

Nitrogen dioxide is a trace gas with important implications in atmospheric chemistry. Measurements of NO_2 are important for the understanding of tropospheric and stratospheric chemistry, its role being known in ozone cycle [1]. In the troposphere, NO_2 is also an indicator of air quality.

There are many measurement methods of the NO_2 concentration: some are in-situ like chemiluminescence, fluorescence, other are remote sensing techniques like DIAL (Differential Absorption Lidar) and DOAS (Differential Optical Absorption Spectroscopy).

Measurements with the DOAS technique [2],[3],[4] are based on Lambert-Beers law which describes the extinction of the solar radiation in an absorbing atmosphere. Measurements with the DOAS technique are divided in two groups: active and passive. In the active measurements the light source is artificial (e.g. a Xe lamp) while for the passive measurements the light sources are natural and these can be: the Sun, Moon or stars.

The DOAS passive method consists in two steps. Firstly molecular absorption cross-sections are fitted to the logarithm of the ratio of the measured radiance and direct solar irradiance without atmospheric absorption. The resulting fit coefficients are the integrated number of molecules per unit area along the atmospheric light path for each trace gas, also called the slant column density (SCD). SCD is converted to a vertical column density (VCD) by ratio of SCD to an air mass factor (AMF) which is influenced by geometry (solar zenith angle (SZA) and line of sight (LOS)), albedo, visibility, and wavelength.

For the NO_2 DOAS measurements many kinds of mobile platforms are used nowadays. Such platforms are: satellites [5], airplanes [6], balloons [7], ships [8], and cars [9], [10]. Dunarea de Jos University of Galati, Romania, and Belgian Insitute for Space Aeronomy in Brussels, Belgium, have a common project under progress for NO_2 DOAS measurements by means of UAVs.

This paper presents NO_2 measurements using a mobile DOAS system performed in the South-East of Romania during two days during the summer months of July and August 2011. The aim of the experiment was to determine NO_2 loading over a large area where different sources for NO_2 exist. To our knowledge, this is the first experiment of this kind made in Romania. DOAS measurements on zenith-sky were performed along more than 300 km on roads which connect the counties of Galati, Braila, and Ialomita.

2 Methodology

2.1 Experimental set-up

Our mobile DOAS instrument consists in one compact Czerny-Turner spectrometer (USB2000, Avantes) with the dimensions 175x110x44mm and 716 g weight installed on a motor vehicle. The spectral range of the spectrometer is 200-750nm with 1.5 nm resolution (FWHM) and the focal length is 75mm. The entry slit is 50μm and the grating is 600l/mm, blazed at 300nm. The CCD detector is a Sony2048 linear array with a Deep-UV coating for signal enhancement below 350 nm, 40 photons per count sensitivity at 600nm and a signal-to-noise ratio of 200. A flexible device (a piece of wood with a hole cached in a small metallic plate), mounted on the top of the motor vehicle, holds the telescope achieving a 2.5° field-of-view with fused silica collimating lenses. The spectrometer is connected with the telescope trough a 400 µm chrome plated brass optical fiber. The spectrometer is connected to a laptop which registers the spectra and at the same time store the position by a GPS receiver. The entire set-up is powered by 12V of the car through an inverter. The spectrometer and the GPS receiver are powered by the laptop USB ports. The entire set-up is shown in Figure 1. Each measurement is a 5-second average of 10 scans accumulations at an integration time between 4 -12ms.

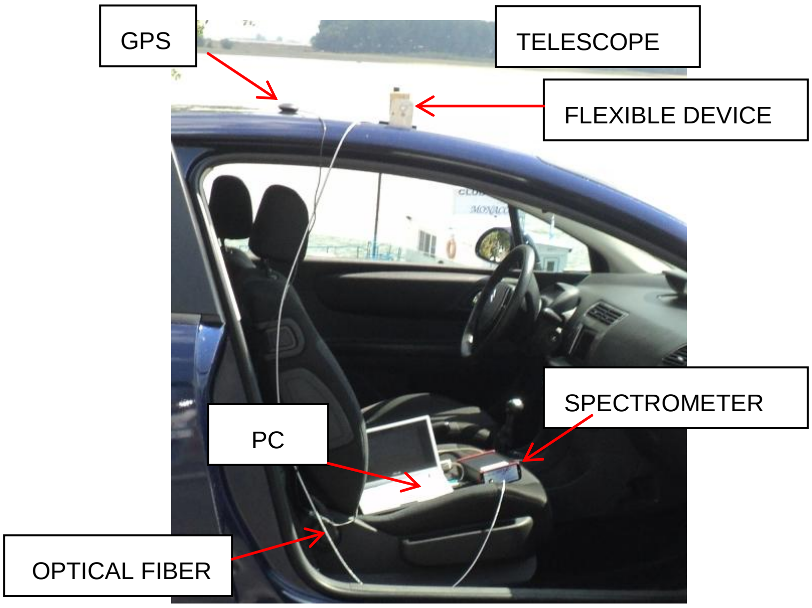
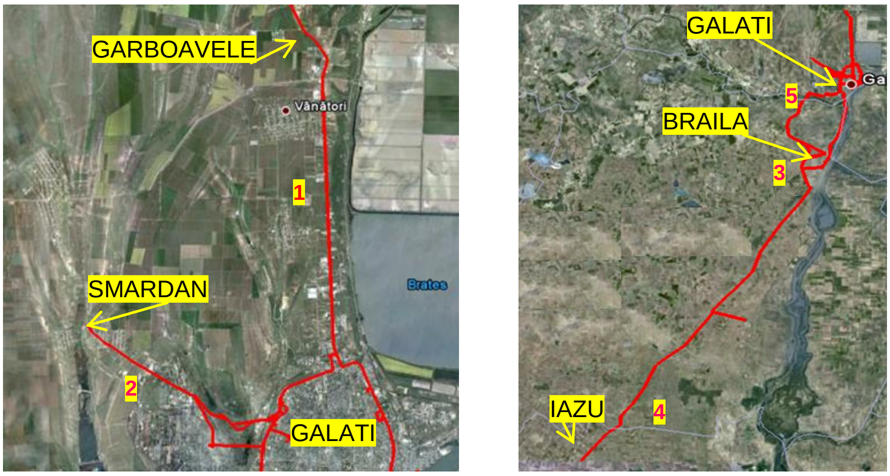


Fig.1 The mobile DOAS system



a) b)

Figure 2 Track measurements on Google Earth with: (a) Galati city. (b) The entire experiment

Mobile-DOAS observations of zenith-sky scattered sunlight were performed during two days with the aim to measure the NO_2 loading in urban and industrial areas and road traffic. The first day of measurements was July 28th, 2011 including five stages. From 09.07 to 09.51 UTC measurements were made in the eastern part of the city along the national road DN26 up to Garboavele forest (45.57°N, 28.00°E). The track of these measurements is indicated with 1 on Figure 2(a). The second stage of measurements (09.55 – 09.85 UTC) focused on the industrial zone between a steel factory and another industrial company along the county road DJ25 up to Smardan village (45.47°N, 27.94°E) – indicated with 2 on Figure 2(a). The third stage of measurements (09.97 – 10.53 UTC) focused next to the city of

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Braila (45.26°N, 27.95°E) along the national road DN22B. The fourth stage of measurements (10.57 – 12.05 UTC) of the experiment focused on the european road E584 from the city of Braila up to Iazu village. The fifth stage of the experiment (12.15 – 13.48 UTC) was back from Iazu(44.73°N, 27.42°E) village to the city of Galati (45.43°N, 28.03°E) on the same track.

The second day of experiments, August 8^{th}, 2011 was dedicated to Mobile-DOAS measurements at different angles. From 05.90 to 5.80 UTC the first set of mobile DOAS measurements were performed at zenith (for approx. 20 minutes), immediately followed by the second set of measurements at an angle of 30° (for approx. 20 minutes). These measurements were performed along the western ring of Galati city.

2.2 DOAS retrieval of NO_2 DSCD

For the analysis of zenith-sky spectra we used QDOAS, a program dedicated to the DOAS retrieval from ground-based and satellite measurements [11]. The NO_2 column density was retrieved in the spectral region 425-530 nm where NO_2 has strong absorption signatures at 439.5, 445 and 448 nm [12]. In the same region strong absorption of O_3, H_2O and O_4 can also be detected. The cross sections of NO_2 [13], O_3 [14], O_4 [15], H2O [16] and a Ring spectrum calculated with QDOAS according to Wagner et al. [17] were included into the fit. A low order polynomial representing the contribution of broad-band absorption in the atmosphere (Rayleigh and Mie scattering) was used in QDOASanalysis. The result of the DOAS fit is a Differential Slant Column Density (DSCD) of NO_2 which is the difference between the NO_2 SCDs of the measured spectrum and the Fraunhofer reference spectrum.

2.3 Deduction of the tropospheric NO_2 VCDs

The result of a DOAS analysis is a DSCD which must be converted to a VCD, which is usually achieved with an AMF calculation. In this paper the deduction of tropospheric NO_2 VCD is done by two methods which yield directly the VCD, the calculation of the AMF not being necessary. This is possible due to the geometrical position of measurements, namely 90° and 30° with the line of sight. We have made the assumptions that scattering occurs above the NO_2 layer. The two methods are presented below and are applied for the measurements of August 8^{th}, 2011.

2.3.1 Method A

The first approach, described by Wagner et al., [18], allowed deduction of tropospheric NO_2 VCD by making the difference between the measurement performed at 30° and the measurement at 90°. This is the simplest method which yields the tropospheric VCD (Figure 7). The equations (1) used are presented below:

$$\begin{cases} Meas_{Zen} = SC_{Strato} + SC_{TropoZen} - SC_{Res} \\ Meas_{Off} = SC_{Strato} + SC_{TropoOff} - SC_{Res} \end{cases} \Rightarrow$$
$$Meas_{Off} - Meas_{Zen} = SC_{TropoOff} - SC_{TropoZen}$$
$$Meas_{Off} - Meas_{Zen} = VC_{Tropo}(AMF_{TropoOff} - AMF_{TropoZen})$$
$$VC_{Tropo} = Meas_{Off} - Meas_{Zen} \tag{1}$$

where:

$Meas_{Zen}$ is the measurement performed in zenith; $Meas_{off}$ is the measurement performed at 30°. SC_{strato} is the stratospheric slant column; $SC_{TropoZen}$ is the tropospheric SC at 90°; SCr_{es} is the residual SC. VC_{Tropo} stands for the tropospheric vertical column.

2.3.2 Method B

The approach used for Method B, also described by Wagner et al., [18], is based on the equations (2) presented below for two measurements made at different elevation angles: 90° (zenith) and 30° (off-axis), concomitantly. Since this approach also yields directly the VCD (Figure 8), calculation of the AMF is not necessary.

$$\begin{cases} VC_{Tropo} = Meas_{Off} - Meas_{Zen} \\ VC_{Tropo} = \dfrac{Meas_{Off} - SC_{Strato} + SC_{Res}}{2} \end{cases} \Rightarrow$$

$$SC_{Res} - SC_{Strato} = Meas_{Off} - 2 * Meas_{Zen} \qquad (2)$$

SC_{res}-SC_{strato} is assumed to vary smoothly in time, and is fitted by a low order polynomial.

Since only one spectrometer was available for this experiment, two different measurements were made, one at 90° and another one at 30°, on the same track in a short time (15 kms in approx. 20 minutes each measurement), making the supposition that the weather conditions and NO_2 concentrations did not change in 20 minutes.

3 Results and Discussions

Figure 3 presents the results of DOAS zenith-sky measurements performed on July 28th, 2011, as described in the introduction of this paper. The high NO_2 DSCD shown on this graphic (~9 – 11 UTC) comes from the cities of Galati and Braila and is the result of measurements in areas with industrial activities or heavy traffic.

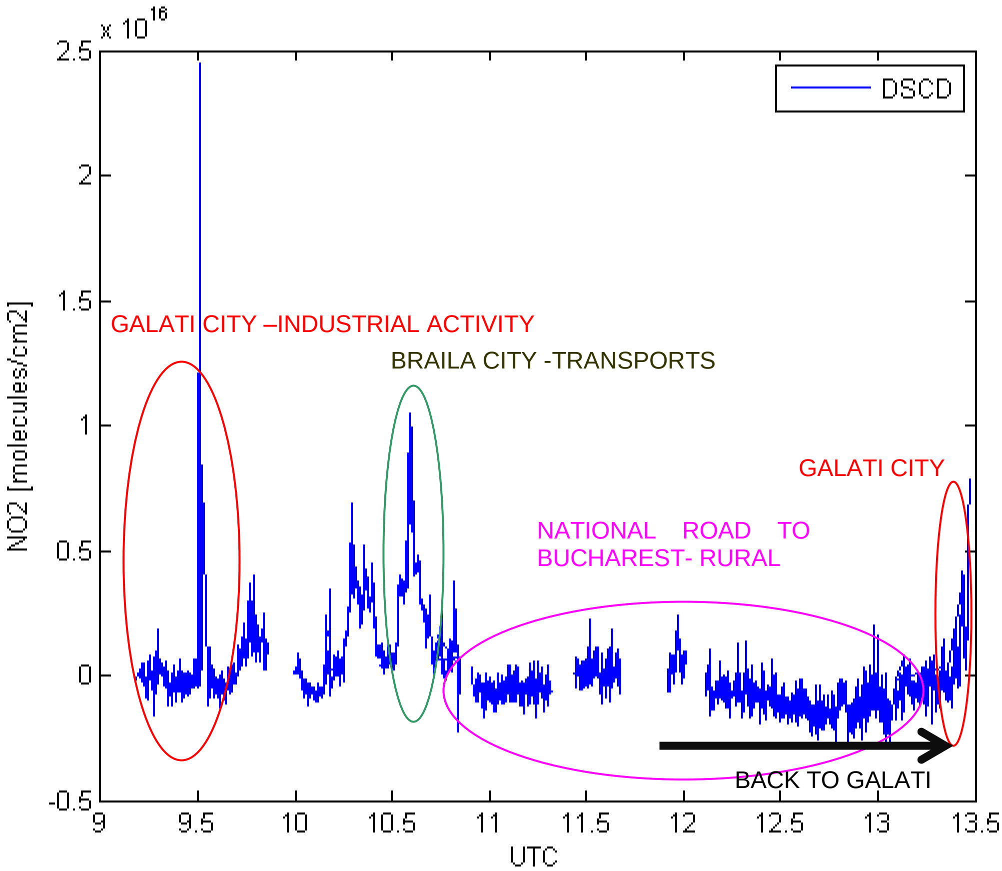

Figure 3. NO_2 DSCD during the round trip (measurements performed on July 28th)

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Figure 4. The NO_2 DSCD in Braila city plotted on Google Earth

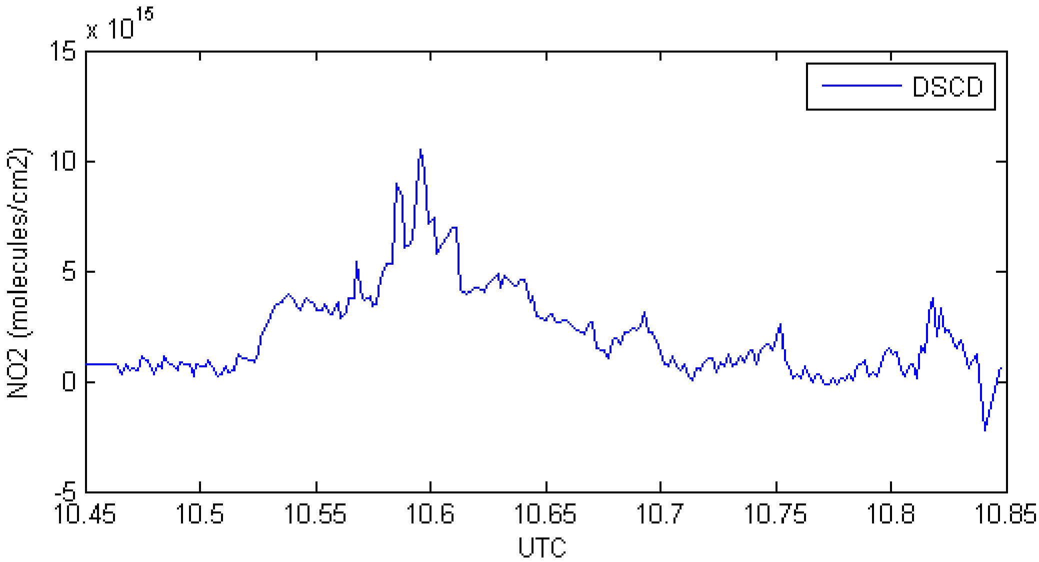


Figure 5. Time series of NO_2 DSCD in Braila city (the same track like in Figure 4)

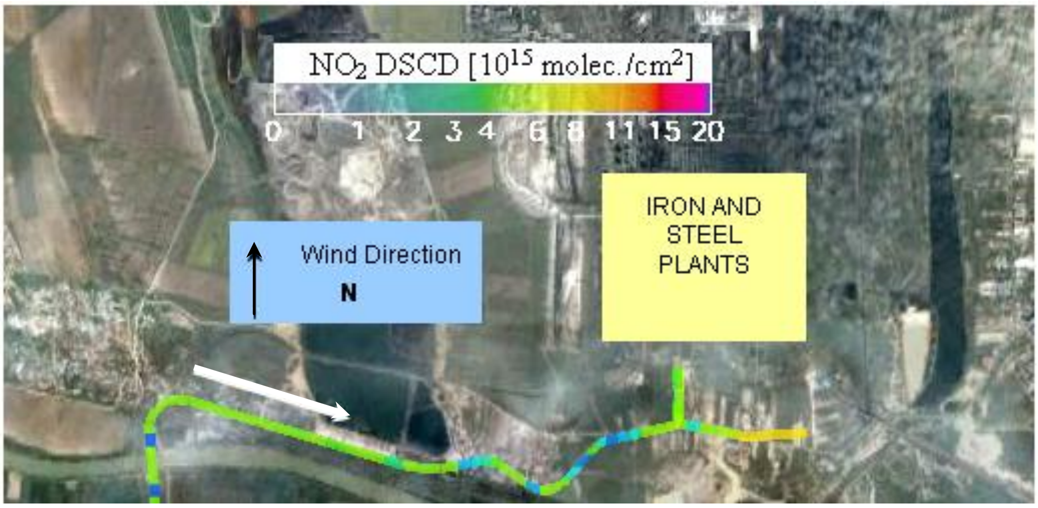


Figure 6. The NO_2 DSCD near the iron and steel plants in Galati city

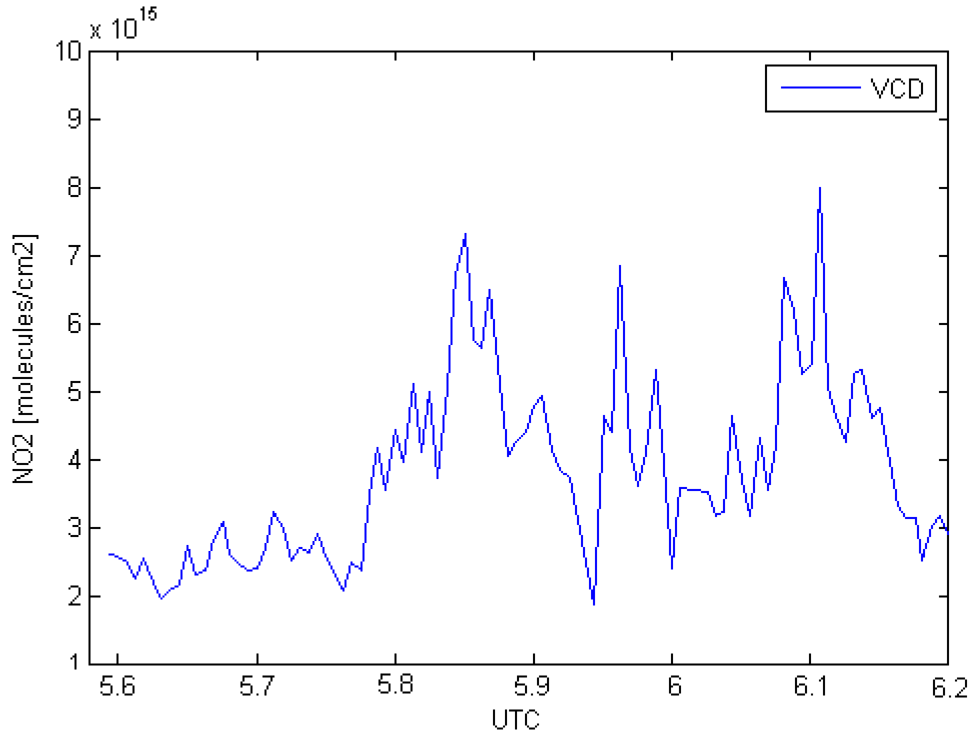
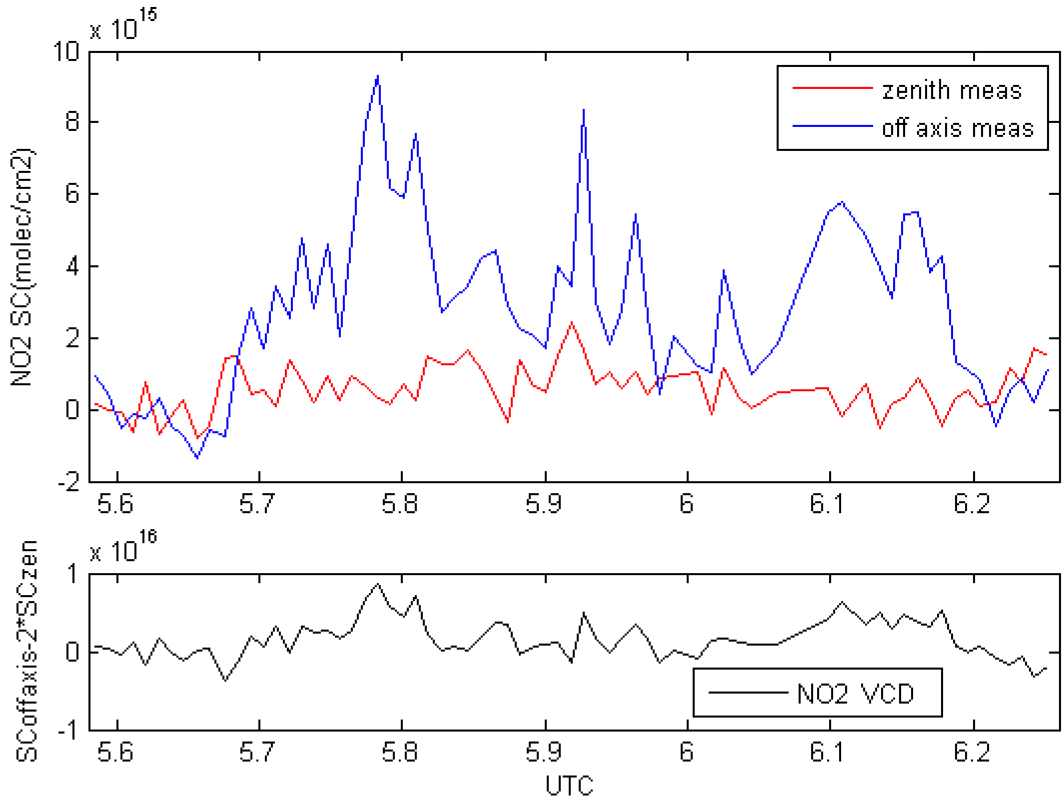


Figure 7. *The NO_2 VCD on the west ring of Galati city obtained using Method A*



Figures 8. The NO_2 VCD on the west ring of Galati city obtained using Method B (the time is an average from both measurements)

In Figures 4 and 5 the case of the city of Braila is presented, which is not known as an industrial city. Parts of the measurements were performed on the national road DN22B and on the European Road E584 passing via the center of the city. This itinerary is usually very used to cross the city as a shortcut to the main exits. It can be assumed that high NO_2 loading detected in the center of the city is caused by the slow heavy traffic.

Figure 6 shows the effects of the wind direction on the variation of NO_2 loading. Before analyzing the spectra we expected to find high NO_2 loading near the iron and steel plants near the city of Galati (the measurement was performed at the very gates of the iron and steel plants). Examining the results obtained and the wind direction it is obvious that the wind has an important role in data interpretation.

The results of measurements performed on August 8th, 2011 at different angles are presented in Figures 7 and 8. Figure 7 presents the result of using Method A where the NO_2 VCD was determined directly. In Figure 8 the result obtained by the use of Method B is presented, the NO_2 VCD being also yielded directly without calculation of the AMF. These cases are the most convenient because of the AMF geometry at 30° and 90°. By use of these approaches are avoided the errors which can occur in the geometric approximations of the AMF. Both methods are useful and have similar results.

4 Conclusions

We presented in this paper an experiment performed on two days of the summer season of 2011 using a mobile DOAS system for measurement of NO_2 in zenith view and at a 30°angle. The experiment focused on areas with potential strong emissions of NO_2 since these are industrial zones or roads with heavy traffic. It is very important that weather conditions should be taken into account and considered in the interpretation of data on NO_2 concentrations and also for mobile-DOAS measurements. Good interpretation of data requires knowledge on wind direction, wind speed, temperature, etc. On July 28th, 2011, we also found that NO_2 coming from road traffic presents high loading especially inside the cities or on the city rings. On the same day of the experiment we also found that the most polluted places are located very close to the industrial zone of Galati city. The center of Braila city, where many vehicles pass, was found with an NO_2 loading close to the loading found near the iron and steel plants. Two approaches for the determination of tropospheric NO_2 VCDs, with similar results, were used by performing measurements at 90° and 30° elevation in Galati city.

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