MOBILE MEASUREMENTS OF NITROGEN DIOXIDE USING TWO DIFFERENT UV-VIS SPECTROMETERS

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Abstract: *The presence of nitrogen dioxide in the entire atmosphere is scarce, yet in lower atmospheric layers the concentration is continuously raising becoming a risk for human health and environment. The main sources for nitrogen dioxide in the atmosphere are related to natural sources and anthropogenic activity. Besides the in-situ measurement techniques (e.g. chemiluminiscence or electrochemical detection) the NO2 abundance in the atmosphere can be studied using remote sensing methods. One of these methods is the DOAS technique which uses sunlight for trace gas detection. This paper aims in presenting the differences of the measurements of DSCD (Differential Slant Columns Densities) for nitrogen dioxide in Bucharest city performed in July 2019 with two different mobile DOAS (Differential Optical Absorption Spectroscopy) remote sensing systems. The mobile DOAS system is basically composed of a mobile platform (e.g. car, airplane, boat, etc.) and a DOAS system (spectrometer, optical fiber, telescope) that gathers spectra from the zenith-sky. One of the systems uses a spectrometer that has the CCD (Charged Coupled Device) detector cooled and one with a spectrometer non-cooled CCD. Results of the study showed that traffic is one of the main sources of pollution in Bucharest and the pollution plume is transported according to wind direction*

Keywords: *Air pollution, Nitrogen dioxide, mobile DOAS, NO_2 DSCD*

1. Introduction

Nitrogen oxides (NO_2+NO=NO_x) are known as a group of chemical species very important in atmospheric chemistry and air quality. In literature NO_x is reported and studied mainly as NO_2 [1]. Naturally is formed in the lower atmosphere by lightning, crops and forest burnings. Lately the concentrations are increasing mainly due to anthropogenic activities like transport and industrial activity [2].

High concentrations of NO_2 close to ground level has a direct effect on materials and human health [3–7].

The study of this important trace gas is made today using several measurement techniques. Most of the measuring techniques involve direct sampling or remote sensing of atmospheric pollution. The DOAS (Differential Optical Absorption Spectroscopy) is one of the most advanced remote techniques used for the study of many trace gases including NO_2 [2]. This remote sensing technique uses natural (sun, moon, stars) or artificial (lamps) sources to produce light which is used as a data collecting vector for the abundance of the trace gases in the lower atmospheric layers (stratosphere and troposphere). DOAS measurements include today remote sensing applications for many trace gases such as NO_2 from ground (ground stations, cars, boats, etc.), air (airplanes, UAV, light airplanes), and space (satellites) [8–13].

In this work, we present the results on NO_2 obtained from concomitant mobile DOAS measurements performed in Bucharest on 18 June 2019 using two types of spectrometer mounted on the same DOAS system.

2. Data and methods

Mobile DOAS observations were performed in Bucharest city on 18 June 2019. We chose for this study Bucharest city (45°26'22″N, 28°2'4″E) because is the largest city in Romania and an important study area for trace gas studies in free atmosphere being chosen for a considering number of research projects and DOAS applications [10, 14]. located in the west part of the city (Figure 1). The steel factory is the main industrial pollution source in Galati city. Other important air pollution sources in Galati are represented by a small power plant and the local traffic.

The position of each DOAS determination was plotted as a map using GIS (Geographic Informational Software). Figure 1 presents the route of the mobile DOAS measurements performed on 18 June 2019 in Bucharest city.

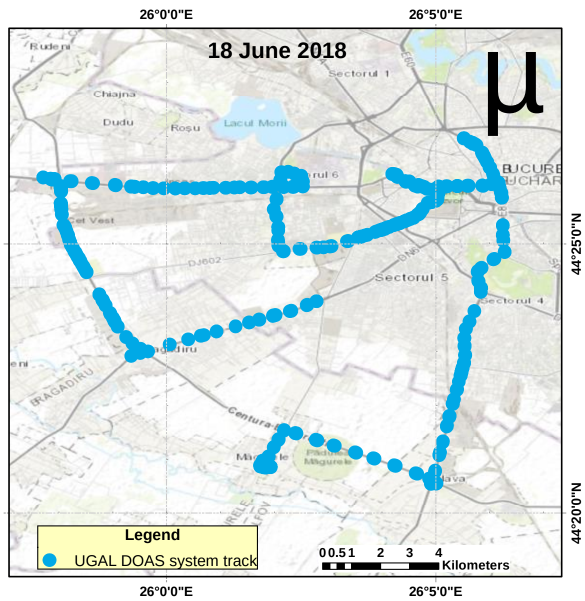

Figure 1: *The route of the mobile DOAS measurements (blue dotted lines) performed in Bucharest on 18 June 2019.*

2.1 DOAS instrumental description

The mobile DOAS instrument presented in this work consists of two compact Czerny-Turner spectrometers from Avantes presented in Table 1. Both of the spectrometers use CCD detector and were placed on-board of a car connected to the same PC (for synchronized spectra recording).

Table 1: Characteristics of the spectrometers used for the mobile DOAS measurements performed in Bucharest on 18 June 2018

Spectrometer/ Code	Number of pixels	Resolution (FWHM) (nm)	CCD detector
AvaSpec-ULS2048x64TEC/ UGAL1	2048	0.4	Pettier cooled
AvaSpec-ULS2048XL/ UGAL2	2048	0.7	non-cooled

Figure 2 presents the UGAL DOAS system set-up composed of two telescopes; two 600 μm optical fibers; two spectrometers; one GPS; one laptop (PC). More details about the instrumental set-up are presented in [15–18].

All measurements presented in this work were performed under clear sky conditions using only zenith-sky observations.

Figure 2: *The UGAL mobile DOAS system*

2.3 Retrieval of the NO_2 VCD

The mobile DOAS observations presented in this work were analyzed using the QDOAS software [19]. The output of the QDOAS spectral analysis is presented as Differential Slant Column Density (DSCD) expressed in molecules/cm^2. Each zenith-sky DOAS recorded spectra were analyzed using the absorption cross-section (spectral prints) of other trace gases and spectral effects in order to eliminate spectral interferences and anomalies. These spectral prints are recorded in laboratories in high resolution using similar conditions found in the atmosphere layers. The cross-sections and settings used in the spectral analysis of this study are presented in Tables 2.

An example of a NO_2 spectral fitting using QDOAS is presented in Figure 3.

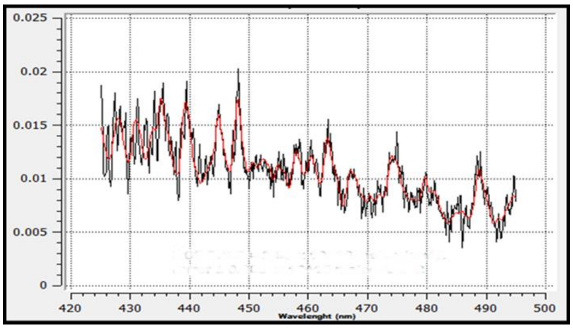

Figure 3: *Example of a DOAS spectral analysis for NO_2 realized with the QDOAS software; the analyzed spectrum was registered on the ring road of Bucharest city. Black lines correspond to the recorded spectra and the red lines correspond to the reference spectra used in the analysis.*

Table 2: DOAS analysis settings used for NO_2 retrieval

NO_2 settings and absorption cross-sections used		
Molecule	Temperature	Reference
NO_2	298 K	[20]
O_3	293K	[21]
O_4	293 K	[22]
Ring	-	NDSC [23]
H_2O	296K	[24]
Wavelength range	425-490 nm	
Polynomial order	5	
Polynomial order	5	

The first step after we obtain the DSCD is to calculate the total slant column density by adding to each determination the value of the density of the reference spectra (SCD_{ref}) used as a setting in the spectral analysis based on:

$$SCD_t = DSCD + SCD_{ref} \quad (1)$$

For conversion of an SCD (Slant Column Density) to a VCD (Vertical Column Density) we need to apply a factor called Air Mass Factor (AMF), which is defined as a ratio between SCD and VCD [2, 25]:

$$AMF = SCD/VCD \quad (2)$$

For noon measurements the AMF can be approximated using a geometrical AMF [25]:

$$AMF(geo) = 1/\sin(\alpha) \quad (3)$$

where α is the Viewing Zenith Angle.

In this work, we estimated the DSCDs as SCDs considering that SCD_{ref} was recorded in a remote area close to mountains where NO_2 sources are scarce. In addition all our measurements were performed close to noon when the sunlight path is shorter and the NO_2 data retrieved is more reliable in determination of tropospheric NO_2 abundance.

3. Results and discussions

In Figure 4 is presented the NO_2 VCD and NO_2 VCD errors retrieved from mobile DOAS observations performed on 18 June 2019 in Bucharest city using simultaneously determinations from using a mobile DOAS system composed of two spectrometers: UGAL1 and UGAL2. Results show that during the measurements both spectrometers detect a comparable variation of NO_2 VCD. The highest NO_2 VCD is detected by both spectrometers around 13 and 14 PM.

From the time series of NO_2 VCD errors presented in Figure 4, we can identify that UGAL1 is more susceptible in detection of higher determination errors of NO_2 VCD due to a non-cooled CCD and having a weaker resolution than UGAL2.

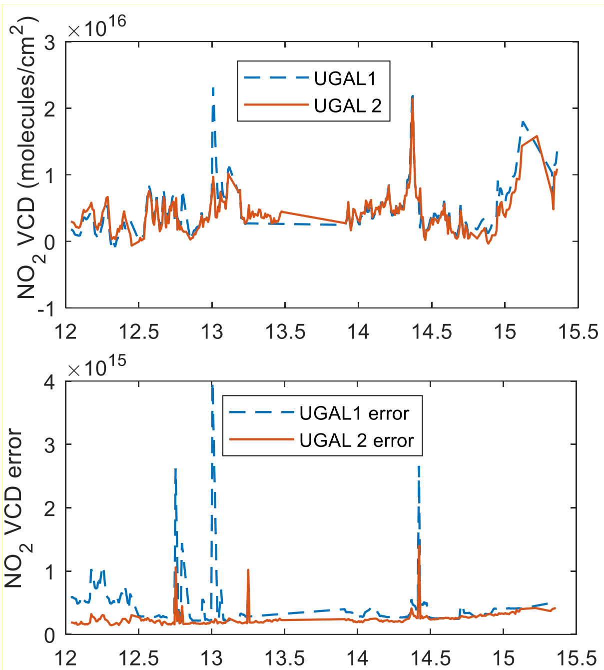

Figure 4: *Comparison between NO_2 VCD (upper graph) and NO_2VCD error (lower graph) retrieved from mobile DOAS measurements obtained using UGAL1 and UGAL2 spectrometers on 18 June 2019*

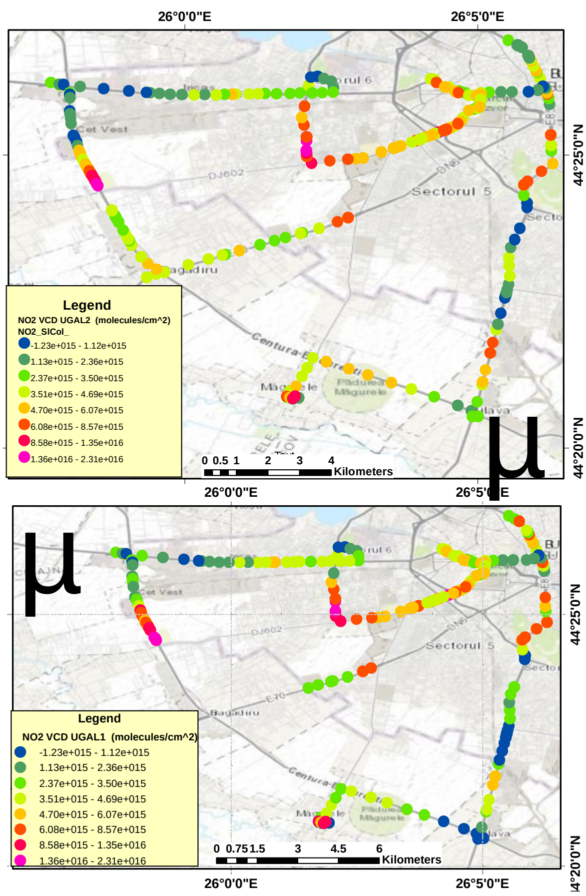

Figure 5: *Color code maps of NO_2 VCD for the mobile DOAS observations performed in Bucharest on 18 June 2019 using two spectrometers: UGAL1 and UGAL2*

The spatial distribution of NO_2 VCD obtained from each spectrometer used in the UGAL mobile DOAS system is presented in Figure 5. We can observe that both spectrometers detected high NO_2 VCD on the main streets and on the western part of the Bucharest city. Also, both spectrometers detected high NO_2 VCD in Magurele city, which was the starting point of our measurement track.

Conclusions

In this work, we presented zenith-sky mobile DOAS observations performed in Bucharest city on 18 June 2019 using a double-channel mobile DOAS system that uses two different spectrometers. The measurements performed are focused on NO_2 detection emitted mainly by road traffic in Bucharest city. The results obtained showed that the mobile DOAS system is a reliable instrument in detection of NO_2 pollution at local level. Both of the spectrometers used can detect similar NO_2 VCD values emitted by local car traffic. Analyze on NO_2 VCD errors showed that UGAL2 spectrometer is more reliable in detecting NO_2 VCD than UGAL1 because it has a more stable detector(cooled) with a higher resolution on recording the sunlight spectra.

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