TROPOSPHERIC NITROGEN DIOXIDE MEASUREMENTS IN SOUTH-EAST OF ROMANIA USING ZENITH-SKY MOBILE DOAS OBSERVATIONS

Adrian Roşu[1], Bogdan Roşu[1], Maxim Arseni[1], Daniel-Eduard Constantin[1], Mirela Voiculescu[1], Lucian Puiu Georgescu[1], Alexis Merlaud[2], and Michel Van Roozendael[2]

[1] *"Dunarea de Jos" University of Galati, Faculty of Sciences and Environment, European Centre of Excellence for the Environment, Domneasca Street, no. 111, 800201, Romania;*
e-mail:daniel.constantin@ugal.ro
[2] *Royal Belgian Institute for Space Aeronomy (BIRA–IASB), Ringlaan–3–Avenue Circulaire, Brussels 1180, Belgium*

Abstract: *Air pollution is an important issue related to human health, quality of life and environment. Nitrogen dioxide (NO_2) and sulphur dioxide (SO_2) are important atmospheric trace gases pollutants. In this study we present zenith-sky mobile DOAS observations of tropospheric NO_2 and SO_2 using a motor vehicle. The measurements were performed in winter of 2017 around Galati city, covering urban, industrial and rural areas. Also, comparisons with the local in-situ observations of NO_2 and SO_2 are presented.*

Keywords: *mobile DOAS, NO_2, SO_2, in-situ measurements*

1. Introduction

Nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) are two important atmospheric trace gases which are used as indicators of air quality. NO_2 and SO_2 form in the lower atmosphere mainly due to anthropogenic activities. The main anthropogenic sources related to fossil fuel combustion in car engines, thermal power stations and industries.

NO_2 and SO_2 have a high impact on human health, e.g. long term exposure can affect the respiratory system of asthmatic children and elderly peoples. High concentration of NO_2 and SO_2 in the lower atmosphere can produce acid rainfall which is one of the primary reasons of deforestation [1].

NO_2 is found in nature as the result of photo-chemical oxidation of NO that can be present in troposphere as a result of lightning storms. A single lightning in the atmosphere produces, due to associated heat, approximately 7 kg of nitrogen into chemically reactive NOx in mid-latitude and subtropical regions [2]. SO_2 can be naturally found in the troposphere as a result of volcanic activities.

NO_2 and SO_2 concentration can be measured using modern techniques such as DOAS (Differential Optical Absorption Spectroscopy), LIDAR (Light Detection and Ranging) and chemiluminescent equipments.

DOAS technique is a method which identifies and quantifies trace gas abundances with narrow band absorption structures in the near Ultraviolet (UV) and visible (Vis) wavelength region in the open atmosphere [3]. This technique can be used to measure gases emitted by point sources as volcanoes, factories, power plants or by area sources (cities) both in stationary and mobile DOAS modes. The mobile DOAS technique can be used onboard of different mobile platforms like cars [4, 5], airplanes [6], UAV (Unmanned Automated Vehicle) [7].

In this study we present mobile DOAS observations used to determine the tropospheric column densities of NO_2 and SO_2 inside and nearby boundaries of Galati city, Romania, performed during 2-4 February 2017.

2. Data and methods

Mobile DOAS observations were performed in Galati city during 2-4 February 2017. We chose as study the area of Galati city (45°26'22″N, 28°2'4″E) because of an important steel factory (Arcelor Mittal) located in the west part of the city (Figure 1). The steel factory is the main industrial pollution source in Galati city. Others important air pollution sources in Galati are represented by a small power plant and the local traffic.

Figure 1 presents the route of the mobile DOAS measurements performed during 2-4 February 2017.

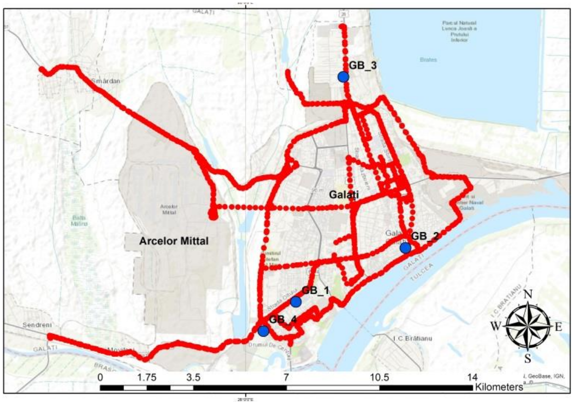

Figure 1: *The route of Mobile DOAS measurements (red lines) and the location of in-situ monitoring stations (blue dots)*

In-situ observations of monitors of the local environmental agency of Galati city (APM Galati) were also available during the period when the DOAS experiments were performed. It was possible to collect the NO_2 in-situ observations freely available online on the website of the national network for air quality monitoring (www.calitateaer.ro). The locations of the in-situ ground based (GB) stations are presented in Figure 1.

2.1 DOAS instrumental description

The mobile DOAS instrument presented in this work consists of a compact Czerny-Turner spectrometer (AvaSpec-ULS2048XL-USB2, of 175 × 110 × 44 mm dimensions and 855 g weight) placed onboard of a car. Figure 2 presents the instrumental DOAS set-up. More details about the instrumental set-up are presented in Constantin et al. (2013).

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

Figure 2: *The UGAL mobile DOAS system*

2.2 Ground-based in-situ data

The local air quality monitoring network is formed by four ground based stations located in different areas of Galati city, as showed in Figure 1. Table 1 presents the type of each monitoring station and its location. The NO_2 concentrations from in-situ monitoring stations are retrieved as hourly mean values from the national network for air quality monitoring. Note that the observations from the national network for air quality monitoring are the subject of future data quality checking, as stated on the air quality monitoring website. For the NO_2 measurements the local air quality network uses “Thermo scientific model 42i NO–NO2– NOx” analyzers, which are based on the chemiluminescence technique.

Table 1: The location and type of each GB station from Galati city

Name	Long. E	Lat. N	Type
GB_1	28°1'4.26"	45°25'77"	industrial
GB_2	28°3'17"	45°25'53"	suburban
GB_3	28°2'2.18"	45°28'22"	urban
GB_4	28°0'23"	45°24'40"	traffic

2.3 Retrieval of the tropospheric NO_2 and SO_2 amount

The zenith-sky spectra presented in this work were analyzed using the QDOAS software [8], using different settings for NO_2 and SO_2. The output of the QDOAS spectral analysis is a Differential Slant Column Density (DSCD). The absorption cross sections and settings used in this study are presented in Tables 2.

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

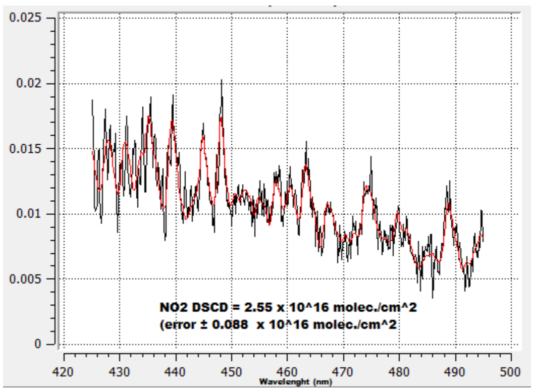

Figure 3: *Example of a DOAS fit of NO2 realized with the QDOAS software; the analyzed spectrum was registered nearby industrial area of Galati city. Black lines correspond to molecular cross-sections scaled to the detected absorptions in the measured spectrum (red lines).*

Table 2: DOAS analysis settings used for NO_2 and SO_2 retrieval

NO_2 settings and absorption cross sections used		
Molecule	Temperature	Reference
NO_2	298 K	[9]
O_3	293K	[10]
O_4	293 K	[11]
Ring		NDSC [12]
H_2O	296K	[13]
Wavelength range	425-490 nm	
Polynomial order	5	
SO_2 settings and absorption cross sections used		
Molecule	Temperature	Reference
O_3	293 K	[10
Ring		NDSC [12]
SO_2	294 K	[9]
Wavelength range	305-325 nm	
Polynomial order	5	

For conversion of a SCD (Slant Column Density) to a VCD (Vertical Column Density) we need to apply a factor called Air Mass Factor (AMF) [14], which is defined as a ratio between SCD and VCD [15]:

$$AMF=SCD/VCD \quad (1)$$

where SCD is expressed as:

$$SCD=DSCD+SCDref \quad (2)$$

where SCDref isthe absorber slant column in the Fraunhofer reference spectrum.

The tropospheric AMF can be calculated using a geometrical AMF [16, 17, 18]:

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

where α is the Viewing Zenith Angle.

In this work we estimated the DSCDs as SCDs considering that SCDref can compensate the stratospheric content, taking into account that the mobile DOAS measurements were performed around noon and the SCDref was recorded in a rural area close to Galati city.

3. Results and discussions

Despite the fact that mobile DOAS measurements were performed nearby some industrial platforms, no important SO_2 source was detected. Thus we will focus in the following on NO_2.

Figure 4 presents the NO_2 DSCD and tropospheric NO_2 VCD retrieved from mobile DOAS observations performed during 2-4 February 2017. The highest tropospheric NO_2 VCD amount (~$8x10^{15}$ molec./cm^2) was detected on 2 February 2017. For the other two days of observations the tropospheric NO_2 VCD detected was ~$4x10^{15}$ molec./cm^2.

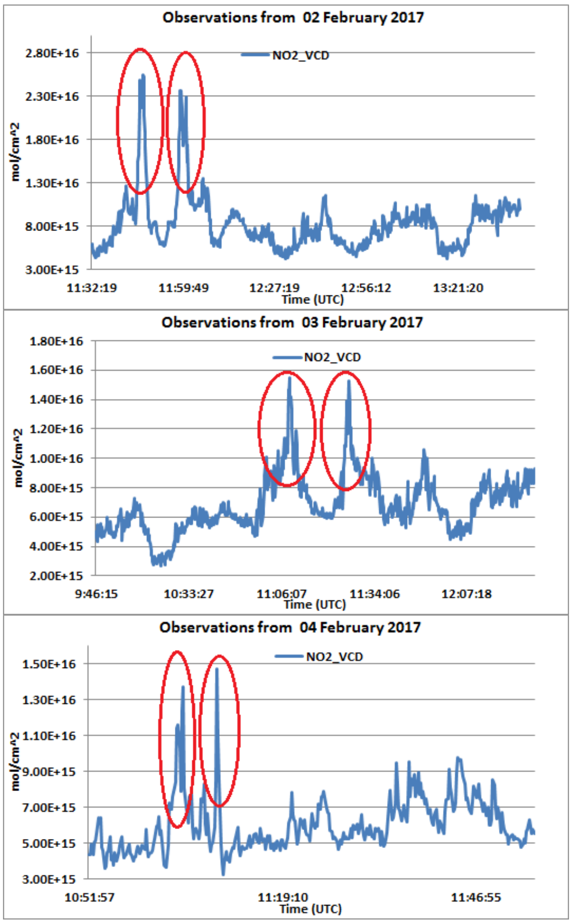

Figure 4: *Comparison between NO_2 DSCD and NO_2 VCD retrieved from mobile DOAS measurements during 2-4 February 2017*

The NO_2 peaks were detected around the industrial platform located in the western part of Galati city (see Figure 5).

Figure 5 presents a color map of the mobile DOAS observations performed during 2-4 February 2017. The plotted measurements show that that the mobile DOAS technique is a useful method and is able to detect the source of air pollution as well as its magnitude. Figure 5 shows that the industrial platform and the local traffic are the main source of air pollution in Galati city.

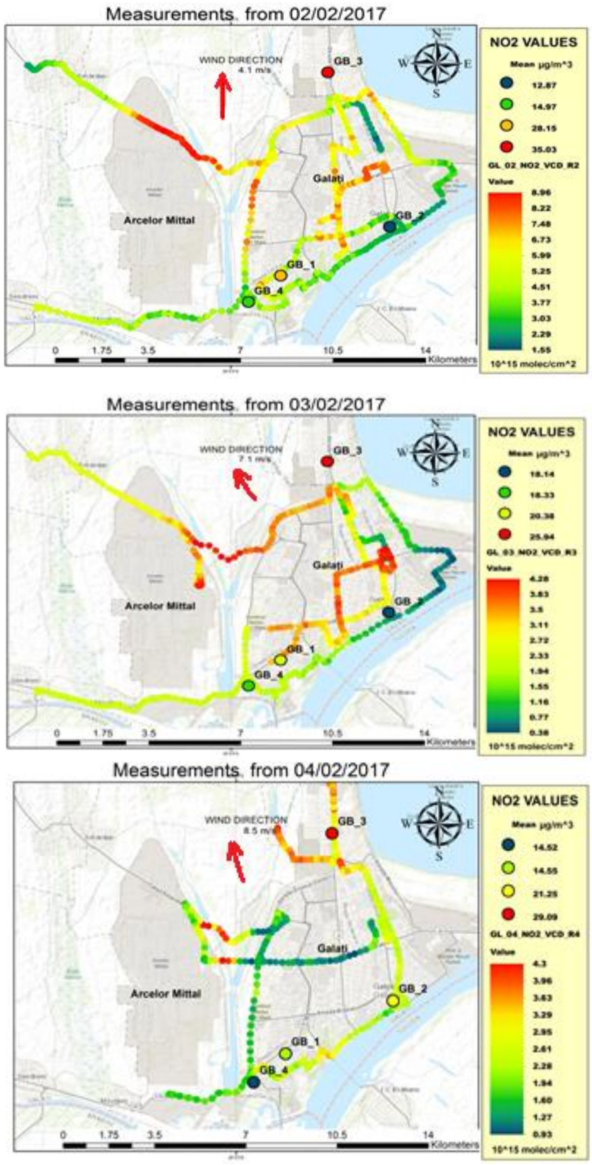

Figure 5: *The color code of tropospheric NO_2 VCD for the mobile DOAS observations performed during 2-4 February 2017 and the ground-based in-situ observations marked by color dots, black bordered*

Also, figure 5 includes the ground-based in-situ observations provided by the local environmental agency of Galati city. A qualitative analysis shows that in-situ ground-based observations support the mobile DOAS measurements, e.g. on the South-East of the city, both DOAS and in-situ measurements show low values. Also, that the highest level of NO_2 is met in the Northern part of the city. During all experiments the wind was blowing from South, thus the main raison for high levels of NO_2 reported on the North part of Galati relates to the steel factory and southern wind blowing on 2-4 February 2017.

Conclusions

In this paper we have presented zenith-sky mobile DOAS observations performed in Galati city during 2-4 Feburary 2017. The measurements focused on NO_2 and SO_2 detection emitted by an industrial platform located nearby Galati city and the local traffic. No SO_2 emissions were observed, thus no information about SO_2 is provided here. The highest tropospheric NO_2 VCD detected by DOAS technique (~$8x10^{15}$ molec./cm^2) was observed nearby the industrial area of Galati city. Also, the in-situ observations, provided by the local network of the environmental agency, support the DOAS observations showing the highest NO_2 concentration where mobile DOAS observations detect high levels of tropospheric NO_2 content.

Acknowledgements: The work of D.E. Constantin and A. Rosu was supported by a grant of the Romanian Authority for Scientific Research and Innovation, CNCS-UEFISCDI, PN-II-RU-TE-2014-4-2584.

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