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# OVERVIEW OF $NO_2$ POLLUTION LEVEL IN THE LOWER DANUBE BASIN DURING DANS MEASUREMENTS CAMPAIGN

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**Abstract**
The aim of this paper is to quantify the $NO_2$level in the lower Danube basin area based on measurements using a mobile DOAS (Differential Optical Absorption Spectroscopy) system. The DOAS system used in this study is composed of an UV-Vis spectrometer for recording the sunlight spectra mounted on a car, as mobile platform. Mobile DOAS measurements were performed in October 2018around and inside the cities of Galati, Braila, Tulcea, in rural areas and remote areas that are far from cities and other major sources of nitrogen oxide, in order to observe how the pollution level varies in the case ofthese zones. The measurement tracks show the $NO_2$ distribution indifferent zones of the lower Danube basin. The values of the $NO_2$ tropospheric densities are extracted from measurements of the mobile DOAS system by using a simple approach. Thus, all the measurements were performed at noon, when the sunlight path is almost perpendicular to the ground surface and therefore, the performed measurements are more sensitive in detecting thevertical column densities (VCD) of trace gases from the troposphere.A GIS (Geographic Information System) software was used to plot the results of the measurements as spatial distribution maps for each track.

***Keywords:*** mobile DOAS measurements, $NO_2$, VCD, GIS

## INTRODUCTION

Nitrogen dioxide ($NO_2$) isone of the major atmospheric pollutants, whichforms the NOxtogether with NO. Nitrogen dioxide isamong the most important molecules inatmospheric chemistry [1].Over the last years, satellite-based observations have provided a better picture ofthe pollution level with $NO_2$, showing that the large cities[2]are the main sources of $NO_2$.The main anthropogenic sources of $NO_2$ areindustry and biomass burning. The $NO_2$ is a brownish, odorless trace gas that is present in the atmosphere mainly due to the burnings of the fossil fuel and due to the lightning occurrence in the lower atmosphere [13]. Also, natural sources such as the microbial activity in the soil contribute to increasing the atmospheric concentration of $NO_2$ [3]. There are several monitoring methods for $NO_2$: chemiluminescence, spectroscopic techniques: DOAS(Differential Optical Absorption Spectroscopy), Laser Induced Fluorescence (LIF), electrochemical sensors and remote sensing (satellite measurements) [4,5].DOAS is one of the most used spectroscopic methods to measure atmospheric trace gases [6]. This method has been used in several specialty studies in different countriesin order to assess the air quality and pollution level on global, regional and local areas.The DOAS technique can be usedfor staticobservations in zenith geometry in order to assess the content of trace gases in vertical atmospheric columns; also,the DOAS instrument can be mounted on different mobile platforms, such as cars, ships, airplanes [7]or UAV (Unmanned Aerial Vehicle)[8]. Examples of measurements using multiple viewing angles (azimuth and elevation angles) were performed, for example, in Mexico City, where mobile mini-DOAS were used to assess the outflow of $NO_2$ and HCHO [9] and trace gases profiles in the atmospheric layers, together with their temporal evolution. MAX-DOAS measurements of tropospheric $NO_2$ and $SO_2$ vertical column densities were made in North China [10]or in Spain for the HONO vertical distribution and their temporal evolution [11].Mobile DOAS measurements were also made byDunarea de Jos University of Galati in Romania,during the measurement campaigns promoted by ESA (European Spatial Agency),such as AROMAT (The Airborne ROmanian Measurements of Aerosols and Trace gases). Parts of the mobile DOAS Romanian measurements are presented in [12, 13, 14].

Within the present study, the $NO_2$ level in the lower Danube basin is assessed, based on measurements of the $NO_2$ column density, as given by the mobile DOAS measurements. The selected region is important for the future coordinated measurements of a large plethora of environmental parameters (including water quality, sediment studies, and biological studies) to be investigated during the implementation of the DANS (Strategy and actions for participation of Romanian teams in the DANUBIUS-RI) project.

## METHODS AND DATA

The mobile DOAS measurements were made in the period between 9 and 11 of October2018,along a distance of 850 km inside and outside the cities of Braila, Galați and Tulcea. The measurements were performed in clear sky conditions between 11 AM and 17 PM. The track of the mobile DOAS measurements is presented in Fig. 1. The DOAS measurements were performed also in remote areas, on main roads around the cities and on the pier of the right bank of the Danube river, located between the town of Isaccea and the I.C. Bratianu commune.

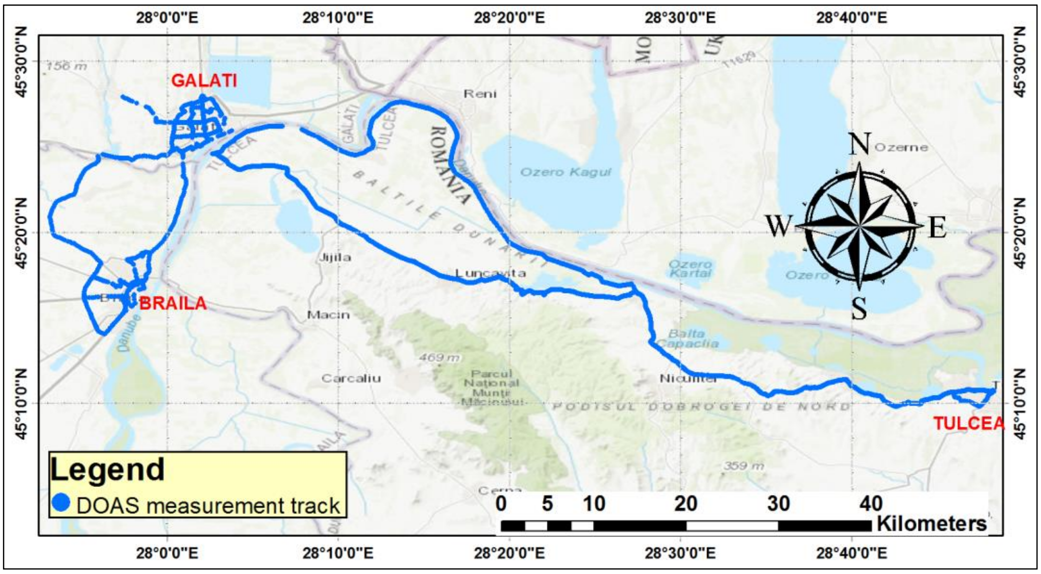


*Fig. 1.Themeasurements track of the UGAL mobile DOAS system conducted in the period between 9 and 11 of October 2018*

The mobile DOAS technique principle is presented in Fig. 2. The Sun’s scattered lightis absorbed by the molecules in the atmosphere;the fraction of absorbed light is proportional to the concentration of the trace gases, therefore the sunlight can be used as a data channel that collects information about the atmospheric composition.The molecule of $NO_2$absorbsthe radiation in the 230 – 600 nm spectral range, with maxima in the 420 – 440 nm region [6].

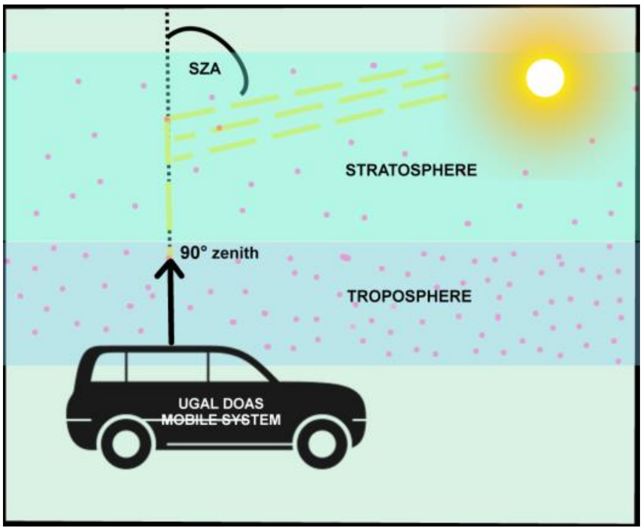


*Fig. 2. The mobile DOAS technique principle applied in the free atmosphere*

The UGAL mobile DOAS system is composed of:a spectrometer (AvaSpec ULS 2048 XL), an optical fiber used to transmit the sunlight to spectrometer (600 µm), a telescope used to capture the sunlight, a GPS (Global Positioning System) used to geo-refer each determination, a PC (laptop) used in storing and analysis of the recorded spectra. All these are mounted on a car, which is the mobile platform (Fig. 3.).


*Fig. 3. The components of UGAL mobile DOAS system*

All the recorded spectra were analyzed with the QDOAS software, developed by researchers at BIRA-IASB (The Royal Belgian Institute for Space Aeronomy) [15]. All measurements were plotted as maps by using GIS (Geographic Informational Software). A series of reference spectra (presented in Table 1) are used for extracting the amount of trace gas, which is expressed as DSCD (Differential Slant Column Densities). An example of $NO_2$ spectral fitting during a spectral analysis can be seen in Fig. 4.

Table 1 The spectral references used in $NO_2$ retrieval

| **$NO_2$ settings and absorption cross sections used** | | |
|---|---|---|
| Molecule | Temperature | Reference |
| $NO_2$ | 298 K | [16] |
| $O_3$ | 293K | [17] |
| $O_4$ | 293 K | [18] |
| Ring | | NDSC [19] |
| $H_2O$ | 296K | [20] |
| Wavelength range | 425-490 nm | |
| Polynomial order | 5 | |

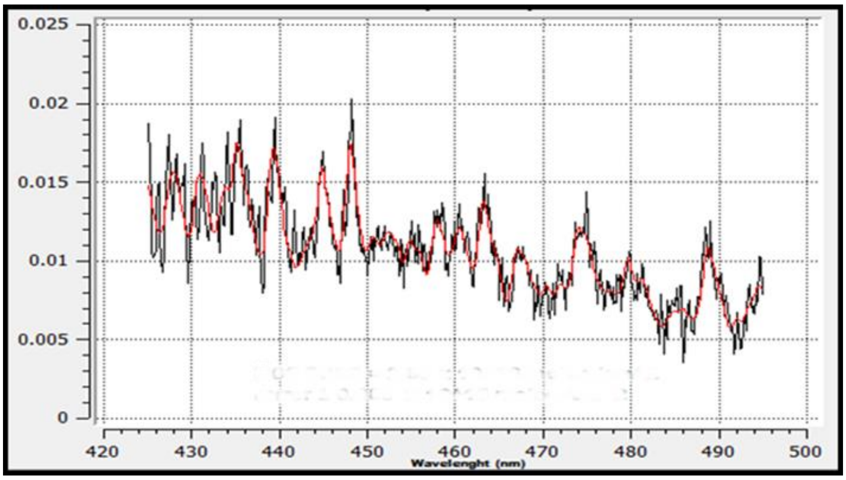


*Fig. 4. $NO_2$ fitting procedure during spectral analysis*

The conversion of DSCD to Vertical Column Densities (VCD) requires a conversion factor called AMF (Air Mass Factor), which is a function including the effects of transmission of light throughout all the atmospheric layers. The AMF we used was calculated by using the following geometric approximation expression:

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

*where α* is the Solar Zenith Angle (SZA)

The $SCD_{ref}$ (the reference spectra) was recorded in a remote area of the Tulcea county,where the pollution with $NO_2$ is very low.The amount of $NO_2$ in the $SCD_{tot}$ (Total Slant Column Density) was quantified by using the following expressions:

$$SCD_{tot}= DSCD+ SCD_{ref} \quad (2)$$

Since all measurements were performed around noon, it is safe to assume that the light path is vertical and thus, the AMF=1 [6]. Using the expression of AMF as a ratio of the slant column and the vertical column densities, we extracted the value of $NO_2$ $VCD_{tropo}$by using:

$$VCD_{tropo} = SCD_{tot}/AMF \qquad (3)$$

## RESULTS AND DISCUSSION

The results of measurements during 9 -11October 2018 are expressed as tropospheric $NO_2$VCD, i.e. the total $NO_2$ molecule density in the vertical column extending from ground to the tropopause.

Fig. 5. presentsthe results of the mobile DOAS measurements performed in Braila and around it expressed as $NO_2$ VCD. High $NO_2$values (1-1.5 x $10^{16}$ molec./cm$^2$) are observed close to the city center. High $NO_2$ values were recorded also on DN 22B, which is one of the main roads that connectsthe cities of Galati and Braila. The main cause of high $NO_2$ values isgiven by the heavy road traffic, mostly from motorized vehicles [21]. The wind direction [22] indicates that the $NO_2$ plume caused by road agglomerations from Braila is transported towards north-east, reaching other areas (see the map presented in Fig. 5). An explanation of the high $NO_2$valuesnear Galati is that the Braila city plume is transportedin the Northern direction towardGalati (see the wind direction from Fig. 5).Another explanation for the increased $NO_2$ signal near Galati could be the fact that the measurements were made at high SZA (70-90), during sunset when the sun is near the horizon and thus, the sunlight path is increased, and therefore more $NO_2$ molecules are accounted for.

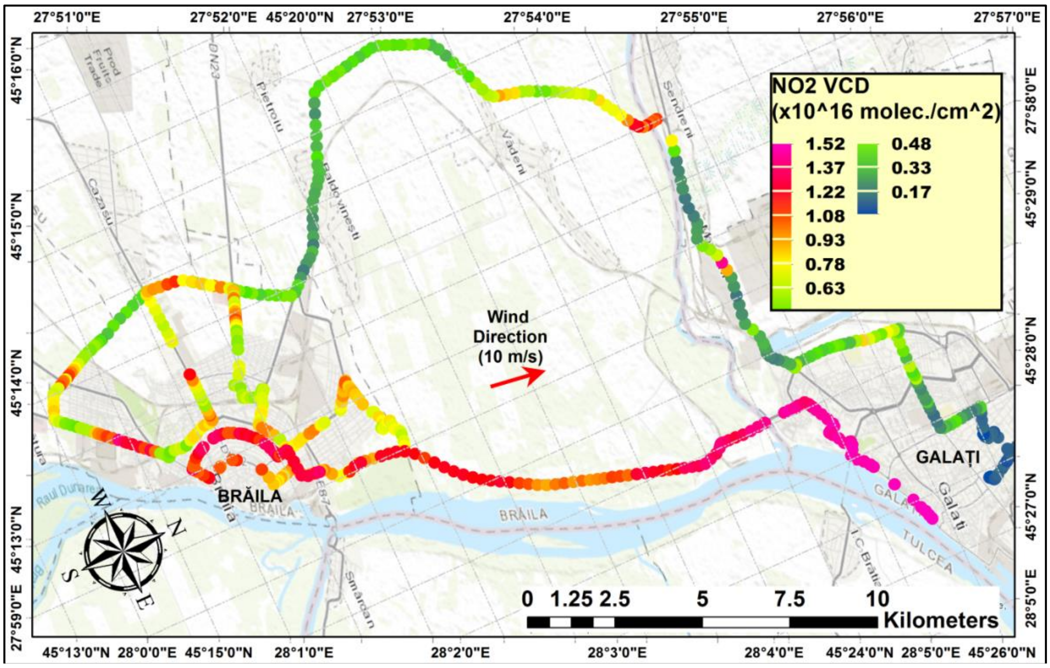


*Fig.5. VCD $NO_2$ from mobile DOAS measurements performed on October, the 9$^{th}$, 2018 in Braila*

Fig. 6. presentsthe $NO_2$ vertical column densities measured in Tulcea County, on October, 10, 2018. High $NO_2$values>2.5 x $10^{16}$ molec./cm$^2$) are seen to the NW, on the E87 road close to I.C. Bratianu village. These increased values may be related to the fact that these are areas where cars wait for the ferry to cross the Danube, usually with their engine on. $NO_2$ values clearly decrease as the UGAL mobile DOAS moves away from these areas and head to Tulcea . $NO_2$ VCD reaches more than 2.5 x $10^{16}$ molec./cm$^2$ on the ring road of Tulcea. Similarly, the cause is the road heavy traffic, but also the main industrial platform from the area, namely Alum S.A., which is located at the entrance in the city. On the returning track to Galati, via the Northern path, the $NO_2$ measurements were made on the pier close to the right bank of the Danube River, in order to see whether possible emissions of the naval transport affect the $NO_2$ level. It was noticed that the $NO_2$ density increases in the neighborhood of the same I.C. Bratianu village. However, one reason may be an artefact, given by high SZA and

more or less by the plume transport from the E87 road traffic.Other possible $NO_2$ sources could be given by the naval transport and the oil refinery, located on the other bank of the Danube River in Moldovia at the confluence of Danube River with the Siret River. To be sure of the naval transport contribution to the detected $NO_2$ pollution plume, it is necessary to usethe DOAS technique onboard of a boat. Future measurements campaign will include simultaneous mobile DOAS measurements on land and on water.

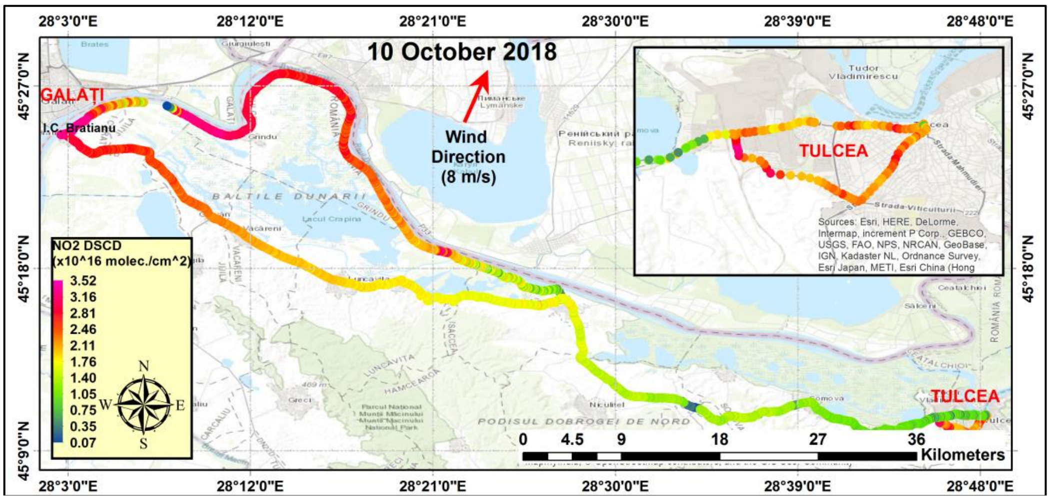


*Fig. 6. VCD NO2 from mobile DOAS measurements performed on October, the 10th, 2018 in the Tulcea County*

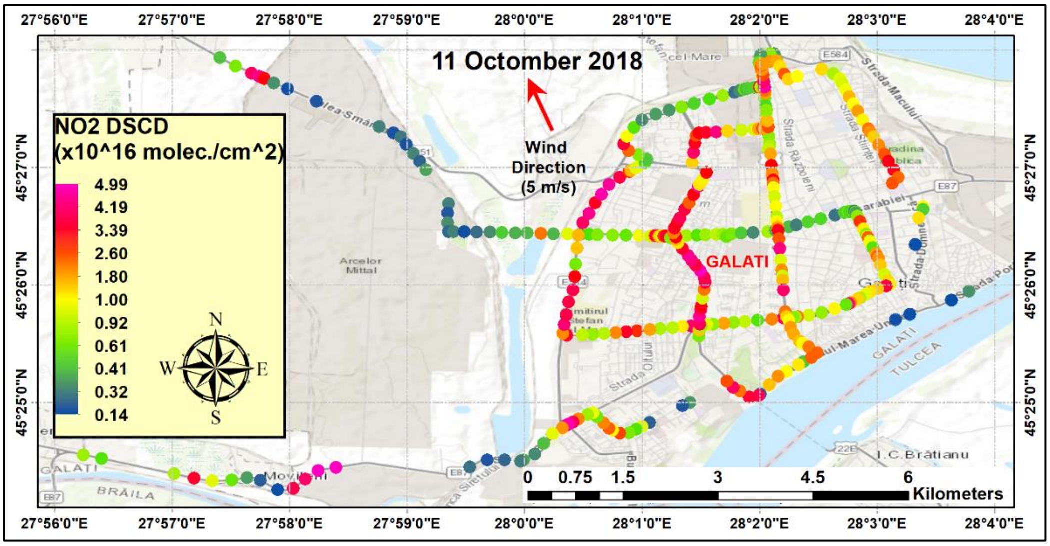


*Fig. 7. VCD NO2 resulted from mobile DOAS measurements performed on October, the 11th, 2018 in Galati*

The tropospheric $NO_2$ VCD measured on October 11, 2018 in Galati is shown in Fig. 7. Much higher values as compared to the previous ones, are reached (4.99 –2.60 x $10^{16}$ molec./cm$^2$) inside the city,at the main streets crossroads, where car agglomerations occur. On the NW track of the mobile DOAS measurements, high $NO_2$ values were recorded. Possibly, the tip of the plume was caused by the main furnace of the Arcelor Mittal industrial platform, located in the Western part of Galati.

## CONCLUSIONS

The mobile DOAS measurements were performed during1-9 of October 2018 over the area ofthe lower Danube basin, an area which is of high interest for environmental studies associated to the DANUBIUS-RI project. Weshowed that the $NO_2$level is heavily affected by the industrial platforms and the car traffic agglomerations. Sources and spatial distribution of the $NO_2$ pollution are similar to other studies [23, 24]. The highest $NO_2$level was detected on the main roads inside the city of Galati, followed by Tulcea and Braila. Any possible effect of naval transport on $NO_2$ level is inconclusive. Consequently, more measurements are needed in the area of the lower basin of the Danube River, in order to isolate other sources of $NO_2$ pollution. Measurements will be done by the DOAS system mounted on board of a boat that will navigate on the course of the Danube River in order to measure the naval transport $NO_2$ emissions.

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