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IMPACT OF SELECTING DIFFERENT REFERENCE SPECTRA ON ERRORS IN DOAS ANALYSIS

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Abstract
This paper presents an analysis of various sources of errors for measurements of atmospheric trace gases concentrations, based on DOAS (Differential Optical Absorption Spectroscopy). The error analysis is based on measurements done in Galati city on 11 October 2018. The spectral window was 425-490 nm which is used for NO_2 detection in the lower atmosphere. Two sets of reference spectra were used: one recorded during a measurement campaign of the project DANS in Galati city and one recorded in May 2015 in a remote area at high altitudes, where NO_2 sources are scarce. This investigation will provide a more reliable method of reducing the errors in NO_2 DOAS spectral analysis by selecting appropriate reference spectra.

Keywords: DOAS technique, mobile DOAS measurements, DOAS analysis, air pollution

1. INTRODUCTION

Nitrogen dioxide (NO_2) is an important trace gas in the atmosphere, which, together with nitrogen monoxide (NO), is known as nitrogen dioxides (NO_x). Trace gasses regulate and participate in many chemical reaction in the lower layers of the atmosphere (stratosphere and troposphere). Nitrogen oxides are very important chemical species that are precursors in formation of ozone trough photochemical reaction [1]. The NO_x has strong influence on the concentration of OH, therefore affecting the lifetime of methane and other gases [2]. NO_2 is a minor trace gas but with an important indirect effect on climate change due to the cooling effect caused by the oxidation of the aerosols produced from burning of the fossil fuels [3]. Ozone destruction is mainly caused by the stratospheric NO_2 that is formed from oxidation of N2O [4]. Stratospheric NO_2 also blocks the depletion of ozone by forming unreactive compounds like $ClONO_2$ and HNO3 [5]. In the troposphere, NO_2 can represent more than 90% of the total column in polluted regions where it's density on column can overpass $3x10^{16}$ molec./cm^2 [6].

Because of the importance of the NO_2 in the atmosphere chemistry and changes that occurs between the atmosphere layers it is important that concentrations and distribution on a global scale are measured on a regular basis, and use accurate methods. Today, observations of NO_2 at global scale are obtained by using equipmenta mounted on satellites alongside with complementary ground based observations, based on DOAS technique (Differential Optical Absorption Spectroscopy), to obtain a clearer image on how much is polluted the air with this trace gas. NO_2 column densities have been retrieved using DOAS technique from space since the mid-90s from the nadir-viewing UV/Vis instruments like: GOME [7], SCIAMACHY [8], OMI [9] and the GOME-2 instruments aboard MetOp-A and MetOp-B [10]. Nowadays, space observations are made with the most advanced space instrument called TROPOMI launched in October 2018 that will extend the record of these observations [11]. In order to sustain and validate these space observations an upwards image of the density of NO_2 columns is needed this is achieved by using airborne and ground based mobile DOAS systems (components of similar system is presented in the next section) during measurement campaigns like AROMAT [12]. Mobile DOAS measurements were recently used over South-East of Europe, to confirm or validate satellite measurements or to identify possible sources and variation of NO_2 pollution [13, 14, 15, 16].

In order to have a reliable support from ground-based measurements detailed tests are needed, as well as evaluation of the results of each step of the retrieval of NO_2 columnar densities. Here we present a preliminary experiment on the first step of retrieval for NO_2 DSCD (Differential Slant Column Densities) by testing how the reference spectra can affect the result of spectral analysis of the mobile DOAS measurements performed in Galati city on 11 October 2018.

2. EXPERIMENTAL

Mobile DOAS measurements were performed in Galati city on 11 October 2018. The DOAS technique is based on Beer-Lambert law applied in free atmosphere, which describes the absorption of the sunlight by the atmospheric trace gasses. In order to perform a spectral analysis it is mandatory to use a high resolution spectral footprint of the trace gas; this is usually recorded in the laboratory in a steady state conditions [17] and an example is shown in Fig. 1. This footprint was used in the spectral analysis where we used the spectra recorded in the window between 425 – 440 nm (red rectangle in Fig. 1).

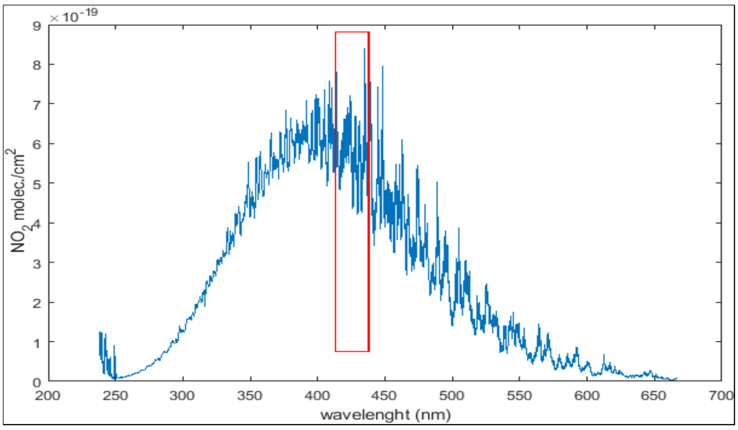
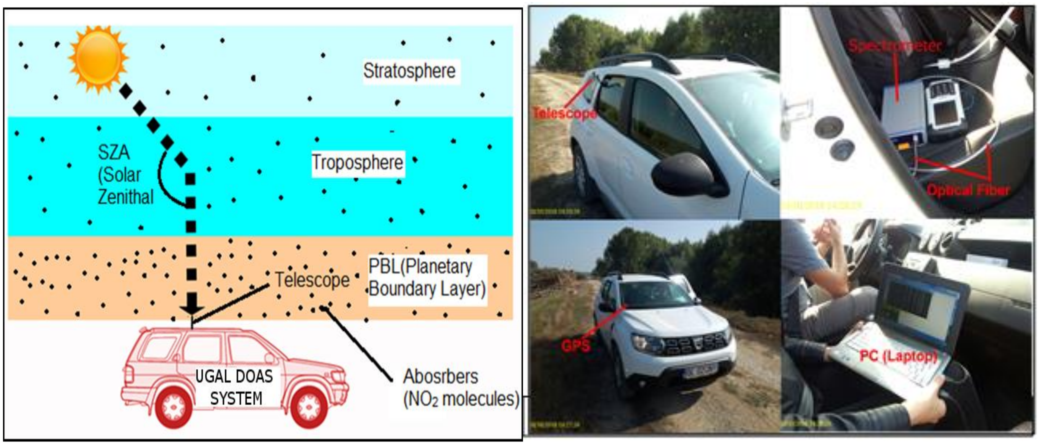


Fig. 1. High resolution for NO_2 absorbtion spectral footprint (cross section bettwen the red rectangle was used as a setting in spectral analisys [17]



a) b)

Fig. 2.a) The principle of mobile DOAS observations; b) The UGAL DOAS mobile system components [14, 15]

The principle of the mobile DOAS method can be seen in Fig. 2a where the mobile DOAS system is recording sunlight spectra in zenith geometry and is mounted on a car. The UGAL DOAS mobile system used in our measurements is shown in Fig. 2b. The car contains the entire DOAS system, consisting of an optical fiber with a telescope mounted on the rear back window viewing the zenith, a GPS (for acquisition of the location of the system), a PC (for spectra recording and data analysis was used a laptop) and a spectrometer (Avantes ULS2048XL Starline, with a spectral resolution of 0.7 nm and a spectral domain ranging from 295 – 550 nm). The whole DOAS system setup can be observed in Figure 2b. Each DOAS determination is spatially referenced using the coordinates recorded by a mouse GPS model BR-355S4. All the data recorded is sent to a PC where the data is stored [13, 14, 15, 16, 18]).

All spectra recorded during the measurement campaign were analyzed using QDOAS software developed by BIRA-IASB (The Royal Belgian Institute for Space Aeronomy) [19]. The NO_2 spectral analysis requires additional information about other atmospheric components (O_4, Ring effect, in order to exclude other spectral interferences, optical and instrumental effects on recorded spectra (see Table 1).

Table 1 QDOAS settings for NO_2 DSCD retrieval

NO_2 **settings and absorption cross sections used**		
Molecule	Temperature	Reference
NO_2	298 K	[17]
O_3	293K	[20]
O_4	293 K	[21]
Ring		NDSC [22]
H_2O	296K	[23]
Wavelength range	425-490 nm	
Polynomial order	5	

One of the most important features in the QDOAS analysis is the reference spectra (SCD_{ref}) (see Fig. 3). The SCD_{ref} is basically a spectrum measured with the same system but assuming that no NO_2 sources exist in the area (i.e. pollution sources). The SCD_{ref} presented in Fig. 3 as a red line was recorded on 1 May 2015, close to Sebeș city in Transilvania, Romania. The other two SCD_{ref} (represented in Fig. 3 as green and bluelines) were recorded on 11 Octomber 2018 in Galati city, at 10 AM and 12 PM local time (LT).

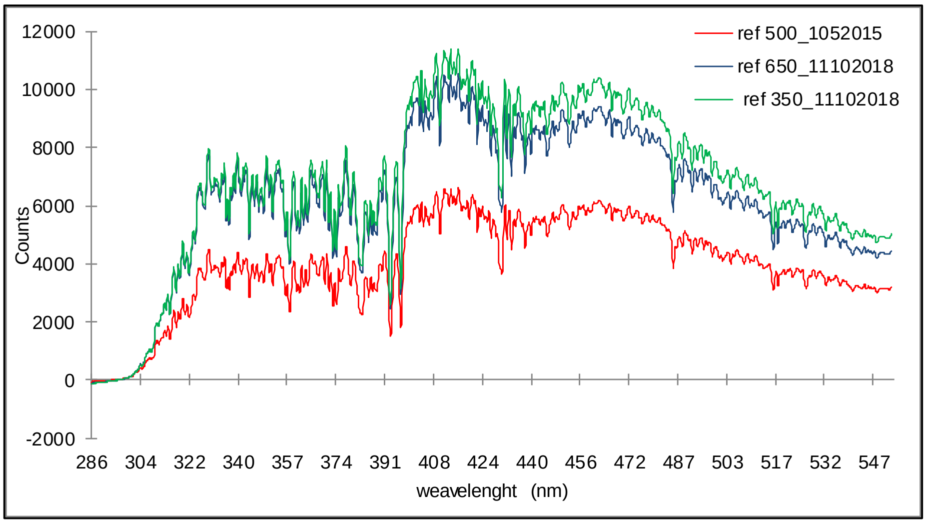


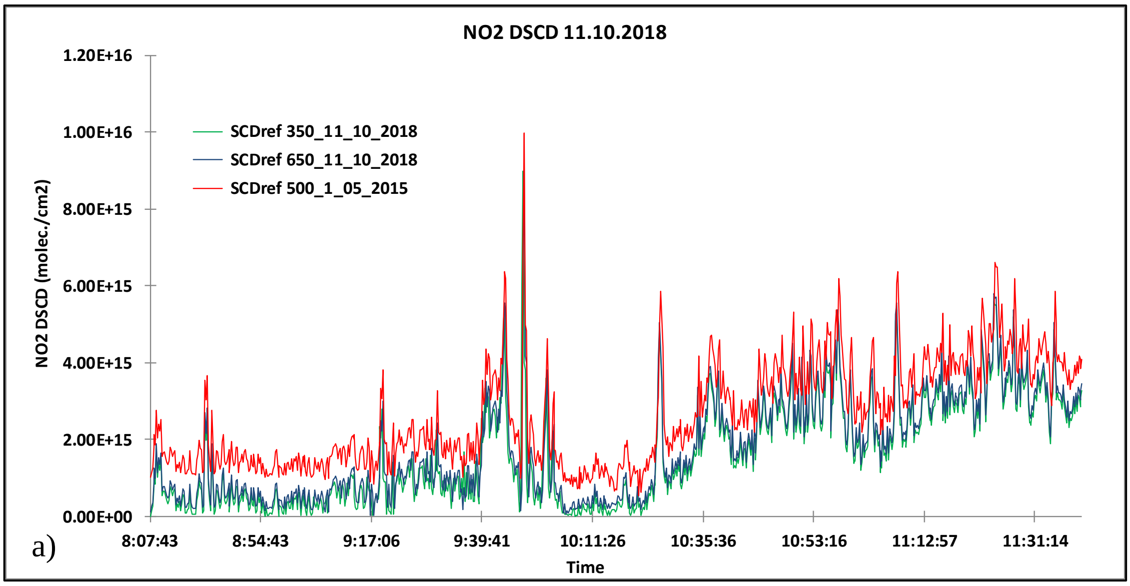
Fig. 3. The three reference spectra used in the QDOAS analisys of mobile DOAS measurement performed in Galați city in 11 October 2019.

The total measured slant column density (SCD_{tot}) is calculated using the following expression:

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

3. RESULTS AND DISCUSSION

The results of our measurements, i.e. the DSCD for NO_2 (a) and the associated errors (b) , are shown in Fig. 4. When a reference spectrum from a remote area is used, the densities are clearly higher, but also the associated errors increase. This is seen mostly during the first period of the measurement (morning), before the spikes most likely associated with traffic increase.



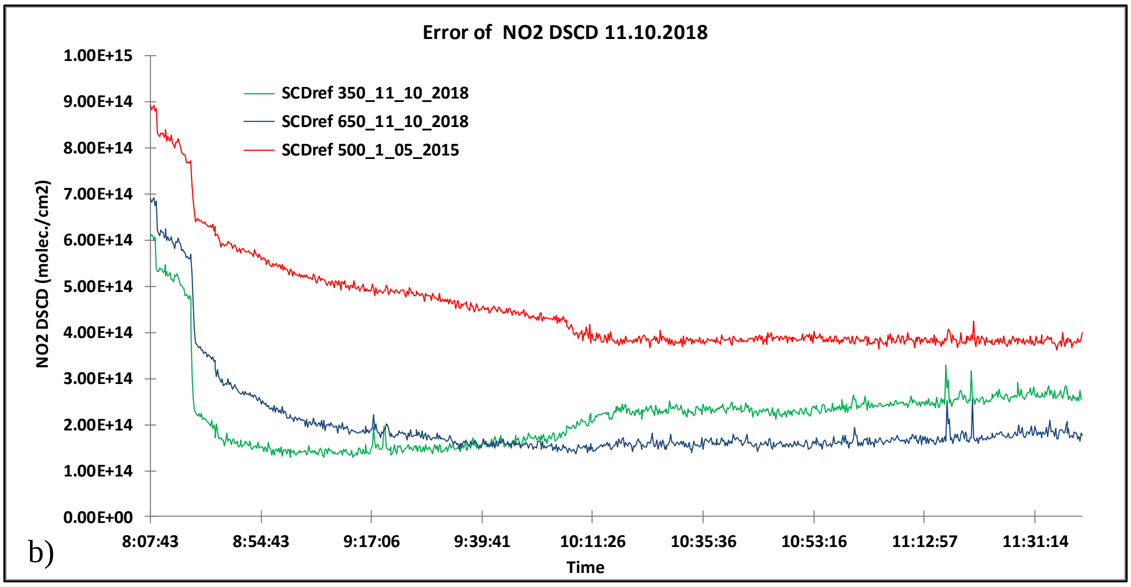


Fig. 4. Results of QDOAS analysis of mobile DOAS measurements performed on 11 October 2018 in Galați city using different reference spectra (results obtained by using SCD$_{ref}$ 500 represented with red line; results obtained by using SCD$_{ref}$ 350 represented with green line; results obtained by using SCD$_{ref}$ 650 represented with blue line): a) NO$_2$ DSCD and b) NO$_2$ DSCD errors.

The error analysis for measurements made on 11 October 2018 in Galati can be seen in table 2. Choosing an appropriate SCD$_{ref}$ will definitely improve the results about the NO$_2$ content given as SCD$_{tot}$ (Total Slant Column Density). Also, using a SCD$_{ref}$ recorded in the same day of the measurements will clearly reduce the error of the NO$_2$ DSCD, especially when measured around noon (12 PM), when the solar light path is shorter

Table 2. Errors of NO$_2$ DSCD resulted from spectral analysis with different refference spectras

SCD$_{ref}$ used in QDOAS analysis	**SCD$_{ref}$ 350**		**SCD$_{ref}$ 650**		**SCD$_{ref}$ 500**	
Date of aquisition	11-Oct-18		11-Oct-18		1-May-15	
Time of aquisition	10:28		12:05		12:02	
Location	Galati		Galati		Sebeș	
QDOAS results	NO$_2$ DSCD	NO$_2$ DSCD error	NO$_2$ DSCD	NO$_2$ DSCD error	NO$_2$ DSCD	NO$_2$ DSCD error
Average	1.64E+15	2.20E+14	1.81E+15	2.01E+14	2.63E+15	4.52E+14
Min	1.03E+12	1.28E+14	1.82E+13	1.38E+14	5.40E+14	3.63E+14
Max	8.99E+15	6.13E+14	9.20E+15	6.91E+14	9.99E+15	8.93E+14
Average Error	13.43		11.10		17.18	
Min Error	7.80		7.61		13.78	
Max Error	6.82		7.51		8.94	

The map of spatial distribution of each DOAS observation made on 11 October 2018 analysed with the SCD$_{ref}$ 650 (which gives the lowest error) are represented in the Fig. 5. Using this method for selecting an adequate SCD$_{ref}$ the mean error for determination NO$_2$ DSCD using spectral analysis is reduced by 10% (case of SCD$_{ref}$ 650). In this way, the spatial representation of NO$_2$ pollution described by NO$_2$ DSCD is more reliable in showing the hot spots in the studied area. The results presented in Fig. 5 show that in Galati city the main sources of NO$_2$ are located on the main streets where traffic jams can occur, another source can be seen in the North-East of the city probably we passed under the emission plume of the steel factory Arcelor Mittal.

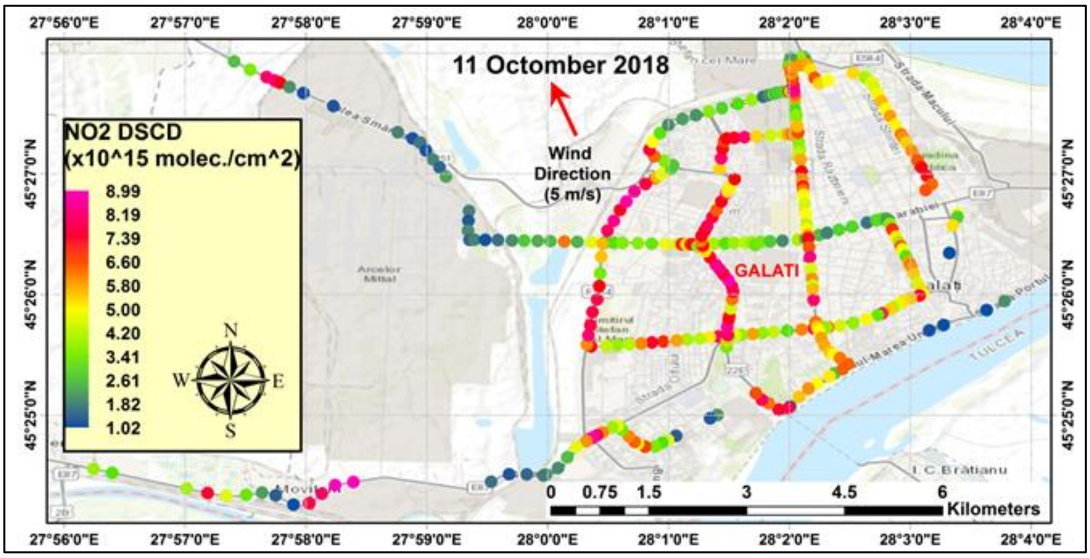


Fig. 5. Distribution map of the NO_2 DSCD resulted from measurements performed in Galati city on 11 October 2018, using SCD_{ref} 650

4. CONCLUSIONS

Results of the spectral analysis based on three different reference spectra shows that using reference spectra recorded in the same day and in the same location reduces the errors of NO_2 DSCD. Unexpectedly, it is not the “cleanest” SCD_{ref} that gives the best results, but reference spectra that originates close to the measurement site. Based on our results we can conclude that using a SCD_{ref} recorded far from the measurements site introduces significant errors, thus reduces the reliability of a correct estimation of the NO_2 pollution level. Using a SCD_{ref} recorded at high SZA (other period that around 12 PM LT, when light is passing almost vertically) can introduce moderate errors in the assumption of the NO_2 DSCD resulted from spectral analysis using QDOAS software.

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